Application for Renewal
of ARB Research Contract No. 2-377

CHEMICAL CONSEQUENCES OF AIR QUALITY
STANDARDS AND OF CONTROL IMPLEMENTATION
PROGRAMS: "ROLES OF HYDROCARBONS, OXIDES
OF NITROGEN, AND AGED SMOG IN THE
PRODUCTION OF PHOTOCHEMICAL OXIDANT"

James N. Pitts, Jr.
Principal Investigator

PROPOSAL APPLICATION FORM

UNIVERSITY OF CALIFORNIA, RIVERSIDE

UCR PROPOSAL NO.

1. SUBMITTED TO: (Agency Name)

State of California
Air Resources Board

FOR AGENCY USE:

Date Received

Number Assigned

2. TITLE OF PROJECT: The Roles of ∧*Hydrocarbons,* Oxides of Nitrogen, and Aged Smog in the Production of Photochemical Oxidant

3A. PROPOSED PROJECT PERIOD		3B. TOTAL AMOUNT REQUESTED	3C. AMOUNT REQUESTED FOR FIRST 12-MONTH PERIOD
From 7/1/73	Through 6/30/74	$113,510	$113,510

4. TYPE OF APPLICATION: Contract __X__ Grant _____

New _____ Renewal of __X__ Continuation of _____ Supplement to _____

5. Scientific field in which this proposal is classified:

Administration ☐ Biological & Agricultural Sciences ☐ Humanities ☐ Social & Behavioral Sciences ☐ Physical Sciences ☒ Education ☐ Other ☐

5A. TYPE OF PROJECT: Research ☐ Training ☐ Public Service ☐ Other ☐

6. PRINCIPAL INVESTIGATOR:

6A. NAME (Last, First, Initial)

Pitts, James N., Jr.

6B. SOCIAL SECURITY NO. of PRINCIPAL INVESTIGATOR

551-22-9719

6C. TELEPHONE NUMBER (Area Code 714)

787-4584 or 787-5124

6D. TITLE OF POSITION: Director, SAPRC, and Professor of Chemistry

6E. DEPARTMENT:

Statewide Air Pollution Research Center

6F. NAME OF COLLEGE, SCHOOL, OR UNIT

University of California
Riverside, California 92502

7. RESEARCH INVOLVING HUMAN SUBJECTS:

A. No __X__ B. Yes, Approved _____

C. Yes, Pending Review _____

8. APPLICANT ORGANIZATION

The Regents of the University of California
University of California, Riverside
Riverside, California 92502
CONGRESSIONAL DISTRICT NO. 43
IRS NO. 95-6006-142 W
PUBLIC, STATE AND EDUCATIONAL INSTITUTION

9. PERFORMANCE SITE(S):

On-Campus Location   Statewide Air Pollution Research Center, University of California,

Off-Campus Location   Riverside

10. INDIRECT COST:

Rate Applicable Under This Project

On-Campus ☒ Off-Campus ☐ __46__% Base __S&W__

Predetermined indirect cost rates approved for the period July 1, 1972 through June 30, 1974.

Congnizant Audit Agency: Department of Health, Education and Welfare.

11. NAME, TITLE & ADDRESS OF PERSON AUTHORIZED TO SIGN FOR INSTITUTION

Ivan Hinderaker
Chancellor
University of California, Riverside
Riverside, CA 92502

Telephone Number 714-787-5535

12. NAME, TITLE & ADDRESS OF OFFICIAL TO WHOM CHECKS SHOULD BE MAILED:

FRANK J. BAILEY
ACCOUNTING OFFICER
UNIVERSITY OF CALIFORNIA, RIVERSIDE
RIVERSIDE, CALIFORNIA 92502

Checks to be made payable to: THE REGENTS OF THE UNIVERSITY OF CALIFORNIA.

13. CERTIFICATION: *The undersigned certify that the statements herein are true and complete to the best of our knowledge. The undersigned further agree to comply with Title VI of the Civil Rights Act of 1964 (P.L. 88-352) and the Regulations issued pursuant thereto. (University of California assurance of compliance filed January 27, 1965.)*

14. SIGNATURES:

14A. Signature of Person Named in Item 6A.

Date March 21, 1973

14B. Signature of Person Named in Item 11.

Date March 21, 1973

UCR-RO   Form P-170 (3/71)

RESEARCH OBJECTIVES

1. APPLICANT ORGANIZATION: The Regents of The University of California
University of California, Riverside
Riverside, California 92502

2. NAME, OFFICIAL TITLE AND DEPARTMENT OF ALL PROFESSIONAL PERSONNEL ENGAGED ON PROJECT, BEGINNING WITH PRINCIPAL INVESTIGATOR:

Name and Title	Department
James N. Pitts, Jr., Director, Professor, Principal Investigator, 10%	Statewide Air Pollution Research Center
Arthur M. Winer, Assistant Res. Chem.	Statewide Air Pollution Research Center
Paul J. Bekowies, Assistant Res. Chem.	Statewide Air Pollution Research Center
John McAfee, Assistant Res. Chem.	Statewide Air Pollution Research Center
George J. Doyle, Associate Res. Chem.	Statewide Air Pollution Research Center
Alan C. Lloyd, Assistant Res. Chem.	Statewide Air Pollution Research Center
William C. Kuby, Associate Professor	Statewide Air Pollution Research Center
(Personnel continued in Section VI)	

3. TITLE OF PROJECT *Hydrocarbons,*

The Roles of ∧Oxides of Nitrogen, and Aged Smog in the Production of Photochemical Oxidant

4. ABSTRACT OF PROPOSED RESEARCH: (Outline Objectives and Methods in 200 Words or Less)

Two distinct air pollution control strategies have been proposed for the reduction of photochemical oxidant to levels specified for 1977 under the amended Federal Clean Air Act of 1970. One is the California (ARB) plan which is based on control of both oxides of nitrogen and hydrocarbons. The Federal Implementation Plan for the South Coast Air Basin, on the other hand, is based upon the assumption of a linear relationship between "high reactive" HC's and photochemical oxidant; oxides of nitrogen are specifically excluded from consideration.

The major objectives of this research are:

1) To provide a sound experimental and theoretical basis for an evaluation of the validity of these two widely differing approaches.

2) To evaluate, as a necessary part of the above task, both existing ambient air quality data and results from past chamber studies.

3) On the basis of an experimentally validated model directed to analysis of the HC/NO_x/O_3-oxidant functional relationship, to predict ambient levels of hydrocarbons and possibly oxides of nitrogen which must be reached if State and Federal Air Quality Standards for oxidant are to be achieved.

4) As an adjunct to our investigation of the atmospheric chemistry of this specific system (HC/NO_x/O_3-oxidant), we will explore the chemical impact of "aged" smog (i.e., remnants of yesterday's photochemical air pollution) on the next day's early morning emission burden, and assess effects on the resulting pollutant levels from the combination of "aged" and "new" smog.

RESEARCH SUPPORT

1. CURRENT SUPPORT: (List All Other Research Support of the Principal Investigator)

Agency and Grant/Contract Number	Title of Project	% of Time on Project	(Direct Costs) Total Award	Period of Support
EPA 800649	Mechanisms of Photochemical Reactions in Urban Air	1 mo. summer	$60,000	12 1/72 – 11 30 73
NSF GP-34524	Chemiluminescent Reactions of Ozone with Organic Compounds	10	$74,444 *	6/1/72 – 5/31/73 (11/30/73)
CAL ARB 2-377	Proposal for a Study on the Chemical Consequences of Air Quality Standards and of Control Implementation Programs	10	$95,519	10/1/72 – 7/1/73
NSF	Gas Phase Oxidations: Kinetic, Mechanistic, and Spectroscopic Studies of Ozone, Hydroxyl Radicals, Oxygen Atoms, and Singlet Molecular Oxygen.	15%	$64,469	7/1/73 – 6/30/74

*Including $13,333 carried forward from ONR-Themis, #N00014-69-A-0200-5001)

2. APPLICATIONS PENDING:

Agency	Title of Project	Total Amount	Period of Support
EPA 800649 (Supplement)	Mechanisms of Photochemical Reactions in Urban Air	$69,007	7/1/73 – 6/30/74
NASA Ames NGR 05-008-029	Airborne Studies of Photochemical Air Pollution in Urban Atmospheres	$24,842	10/1/72 – 3/31/73
NSF-GP-34524 (Supplement)	Chemiluminescent Reactions of Ozone w/Organic Compounds	$28,880	6/1/72 – 5/31/73 (11/30/73)
EPA (G. J. Doyle, Co-investigator) ** See below	Determination of the Spectral Distribution of Absorption Cross-Section of Aerosols in Polluted Atmospheres in the Infrared, Visible, and Near Ultraviolet Regions	$40,000	7/1/73 – 6/30/74

3. DUPLICATE APPLICATIONS:

This application is also being submitted to other agencies for consideration.

YES_____ NO____X_____ (If YES, state to whom, date, amount and period)

Agency	Date	Total Amount	Period of Support
** Applications Pending (continued)			
NSF-RANN	Chemical Transformations in Photochemical Smog and Their Applications to Air Pollution Control Strategies	$999,090	10/1/73 – 9/30/75

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I. PROPOSED RESEARCH PROGRAM

A. Introduction and Statement of the Problem

Although a great deal of data relating oxidant levels in chambers to initial
concentrations of hydrocarbons (HC) and oxides of nitrogen (NO_x) has been accum-
ulated during the past two decades, considerable uncertainty continues to exist
concerning the roles and relative contributions of HC and NO_x in the formation
of photochemical smog. The lack of knowledge concerning the precise functional
dependence of oxidant formation on HC and NO_x levels has led to conflicting
positions by regulatory agencies as to the most efficient emission control strat-
egy that would lead to achievement of federal and state ambient air quality
standards. This situation has serious technical, social, and economic implica-
tions.

For example, the EPA implementation plan for the California South Coast Air
Basin presented on January 15, 1973, proposes imposition of drastic levels of
gasoline rationing during the months of heavy smog. This control strategy is
based upon the assumption that the yearly high one-hour ambient oxidant reading
for a given day is directly proportional to the amount of "high reactive hydro-
carbon emissions" for that day. It is significant that this assumed straight
line proportionality between ambient oxidant reading and reactive hydrocarbon
inventory fails to include any consideration of the role of oxides of nitrogen
in determining ambient oxidant levels. Serious objections can be raised to
this approach since a considerable body of relevant smog chamber data (see
Background Section which follows) supports the conclusion that oxidant formation
is dependent in part not only on reactive hydrocarbons but also on the concentra-
tion of oxides of nitrogen.*

Clearly, there is an urgent need to clarify the issue of whether reduction
of only reactive HC, or both reactive HC and NO_x, is required in order to achieve
the ambient air quality standard for oxidant. Further, the problem requires
quantification of the degree of reduction(s) necessary to reach the air quality
standard.

The need for a detailed experimental investigation of this problem was
spelled out in a letter of March 1, 1973, from Mr. Dale Hutchison, Chief of the
Air Resources Board Research Section, to the Principal Investigator. He specified
the following research tasks:

1. "An experimental program to determine whether the EPA's model
    of photochemical smog is correct or whether the ARB's model

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*
It should be noted here that the term "reactive" hydrocarbons has sometimes been
used in misleading and ambiguous ways. In this proposal, unless otherwise noted,
hydrocarbons or "reactive hydrocarbons" will be taken to mean all non-methane
hydrocarbons, since it has become clear that certain hydrocarbons formerly charac-
terized as "unreactive" will actually produce substantial amounts of ozone given
sufficient time to do so (i.e. irradiated propane-NO_x mixtures in air).

of photochemical smog is correct. The EPA's photochemical model is that only reactive hydrocarbons need to be reduced while the ARB's model is that both non-methane HC's and NO_x need to be reduced in order to achieve the air quality standards. An experimental program to determine which model is correct will be particularly helpful."

2. "After a correct model has been defined, an experimental program should be designed to determine how much reduction is necessary to achieve ambient air quality standards. This can be undertaken by reducing the first HC and then NO_x or perhaps reducing both together. The reduction schedule should be related to the reductions expected from the implementation plan."

3. "It is important to understand the reactions of today's emissions with yesterday's smog."

Accomplishing these research tasks clearly will require more appropriate and quantitatively valid data than presently exist. We believe that the new SAPRC smog chamber facility, funded by the Air Resources Board, provides a unique means of acquiring such kinetic and mechanistic data. Furthermore, we feel that in order to answer questions 1-3, the acquisition of such experimental data must be accompanied by a careful evaluation of existing data and the inclusion of both existing and new experimental data into a valid, workable model for the formation of photochemical oxidant in chambers, and ultimately in ambient air. The latter requirement is highly compatible with the chamber program to be conducted concurrently for the EPA which has as its goal refined computer modeling of fundamental chamber data. The two programs will be strongly and mutually reinforcing.

As indicated by Mr. Hutchison, an adjunct to the problem of determining a correct model of the functional dependence of oxidant formation on HC and NO_x levels, is the elucidation of the role and influence of products remaining from "yesterday's" photochemical reactions on smog formation originating from "today's" emission burden. Again, it is felt that the SAPRC chamber facility offers an opportunity to simulate the process by which slow reactions and other products surviving through the night are included in the matrix of freshly polluted morning air which subsequently undergoes photolysis. Comparison of results for controlled systems both with and without remnants of yesterday's products could lead to clarification of their role in photochemical air pollution in areas such as the South Coast Air Basin which are subject to periods of static wind conditions accompanied by strong inversions.

In the following section, we summarize the results of relevant chamber experiments conducted during the past decade in a variety of laboratories. We then define the overall objectives and specific aims of our research program designed to answer the specific questions put forth by the ARB. This is done in part by extending the efforts of previous workers into the very dilute concentration domain more nearly conforming to present and anticipated levels of primary pollutants. Finally, we present a detailed technical plan specifying the methods of procedure by which the research program will be carried out.

Due to the critical and difficult nature of the questions being posed here by the ARB, we will review this proposal in depth at a conference at the SAPRC prior to the start of this contract. The purpose of this meeting will be to fully utilize the expertise of the members of the Air Resources Board and its technical staff and the ARB Chamber Scientific Advisory Committee in a detailed, critical evaluation of our proposed research program. At that time, if necessary, it will be possible to recast detailed elements of our experimental plan to take advantage of the latest information concerning the major questions being dealt with in this proposal.

B.   Background and Previous Research

Chamber Studies

Although it has been over 20 years since Haagen-Smit (1956 and papers cited therein) established that photochemical smog results from the ultraviolet irradiation of hydrocarbons and oxides of nitrogen, the effectiveness of reducing the absolute amounts of either or both of these reactants, and/or their ratios, as a means of reducing oxidant production remains uncertain.

Two general approaches to deciding on an effective control strategy for photochemical oxidants have been taken. The EPA has established a federal air quality standard for non-methane hydrocarbons (0.24 ppm C for 3 hours, 6-9 a.m.) deemed to be adequate to allow the health related air quality standard for
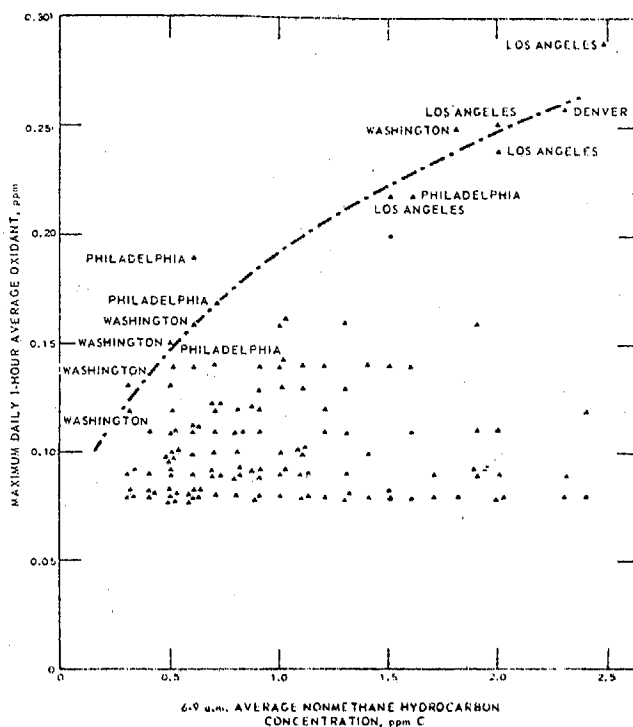
Figure 1.   Maximum daily oxidant as a function of early morning non-methane hydrocarbons, 1966-68 for CAMP stations; May through October 1967 for Los Angeles (USDHEW, 1970)

oxidant (0.08 ppm for 1 hour) to be met. This decision was based on an evaluation of the ambient oxidant levels as a function of early morning non-methane hydrocarbons (USDHEW, 1970), (see Figure 1). More recently, the EPA (1973), in their proposed control strategy to meet the Federal oxidant standard in the South Coast Basin, has stated, ". . . a straight line proportionality is assumed to exist between the ambient oxidant reading and the high reactive hydrocarbon inventory."

The California Air Resources Board has taken the position that effective reduction in photochemical oxidant levels requires control of both hydrocarbon and oxides of nitrogen. This position is based on a number of experimental smog chamber studies in which a variety of smog symptoms (eye irritation, total oxidant levels, rate of nitrogen dioxide production, etc.) were measured as a function of initial concentrations of hydrocarbon and NO_x.

A comparison of several of the earlier studies of this type has been made by Hamming and co-workers (Hamming and Dickinson (1966) and papers cited therein) and by Nicksic, Harkins and Painter (1966). For example, the severity of eye irritation as a function of both hydrocarbon and NO_x levels may be shown in a contour plot such as Figure 2 (Hamming and Dickinson, 1966). This type of plot shows clearly that eye irritation depends not only on the hydrocarbon concentration but on the $HC:NO_x$ ratio and that an effective control strategy will depend on where the starting point (i.e., current hydrocarbon and nitrogen oxides levels) falls on a plot of this type.

Although large amounts of data relating oxidant levels in chambers to initial hydrocarbon and nitrogen oxide concentrations have been gathered during the past two decades, only a small portion of this data is pertinent and applicable to the program of satisfying the standard for oxidant. Data from studies using pure organic compounds, NO_x and air, although valuable for elucidation of mechanism and for relative ranking of compounds for "smog potential" cannot be used until a more reliable, usable, and generally applicable model has been developed and verified for the chemical and physical transformation involved in the formation of photochemical oxidant in simulated and real ambient air.

The more pertinent features of studies of these simpler systems are summarized below. This is followed by our evaluation of the more pertinent smog chamber studies of those systems which simulate more accurately the complex mixtures found in real polluted atmospheres.

Altshuller and co-workers (1969) carried out smog chamber studies of n-butane-NO_x, or n-butane-ethane-NO_x mixtures with varying amounts of propylene or toluene added. They found:

"Exclusion of olefins and alkylbenzenes was highly effective in reducing oxidant dosage, formaldehyde and peroxyacetyl nitrate concentrations, and eye irritation response. The only penalty was a modest increase in nitrogen dioxide dosage. A large reduction in nitrogen oxide concentration reduced nitrogen dioxide dosage and eye irritation response, but with the penalty of a large increase in oxidant dosage."
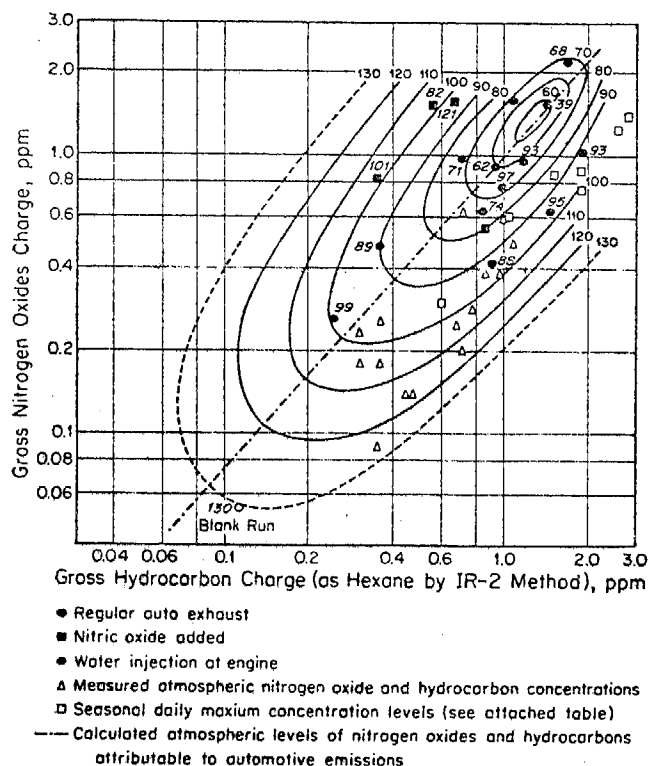
Figure 2. Variation of eye irritation response with primary concentrations of auto exhaust and nitrogen oxides. Data are for 4
hours irradiation, and are from Air Pollution Control District-
California Department of Public Health contract studies.
(Hamming and Dickinson, 1966)

The reduction in nitric oxide concentration was from 1.2 to 0.3 ppm; the concomitant increase in oxidant for 3 ppm n-butane was from 0.05 to 0.9 ppm. This
lower level of nitric oxide (0.3 ppm) is about that observed in unreacted
ambient air (Stephens and Burleson, 1969). At this level, Altshuller et al.,
found that addition of 0.5 ppm of propylene and of 1.5 ppm of toluene to 3 ppm
n-butane produced a slight decrease in maximum oxidant level but an increase
in oxidant dosage. The lower concentration ranges employed in this study
correspond to the current atmospheric levels of NO_x; thus, conclusions reached
in this study are not directly applicable to the evaluation of the effects of
future reductions in ambient NO_x levels, except by extrapolation.

A number of studies on the photochemical reactivities of single hydrocarbon-
NO_x mixtures have been carried out. Glasson and Tuesday studied the rate of NO
oxidation by several olefins and aromatics, e.g., o-xylene, mesitylene and n-
hexane (1970b), and found that for certain of these hydrocarbons the relative
reactivity is dependent on the concentration. Thus, the rate of oxidation of
NO in the UV irradiated system, mesitylene-NO_x-air is twice that of the system
propylene-NO_x-air when the HC concentrations are 0.25 ppm, but mesitylene is
only one half as effective as propylene when the HC concentrations are 5.0 ppm.

Glasson and Tuesday (1970a) studied the effect of NO concentration on the rate of hydrocarbon disappearnace, or product formation, as monitored by LPIR spectroscopy for several olefins and m-xylene. Typical results for single hydrocarbons are shown in Figure 3; results for a mixture whose composition was intended to simulate that of polluted air are shown in Figure 4. The maxima in these curves are of interest because they are in direct contrast to curves generated by Dimitriades (1970) from irradiated auto exhaust. The latter (see Figure 6) do not show maxima corresponding to those found by Glasson and Tuesday.
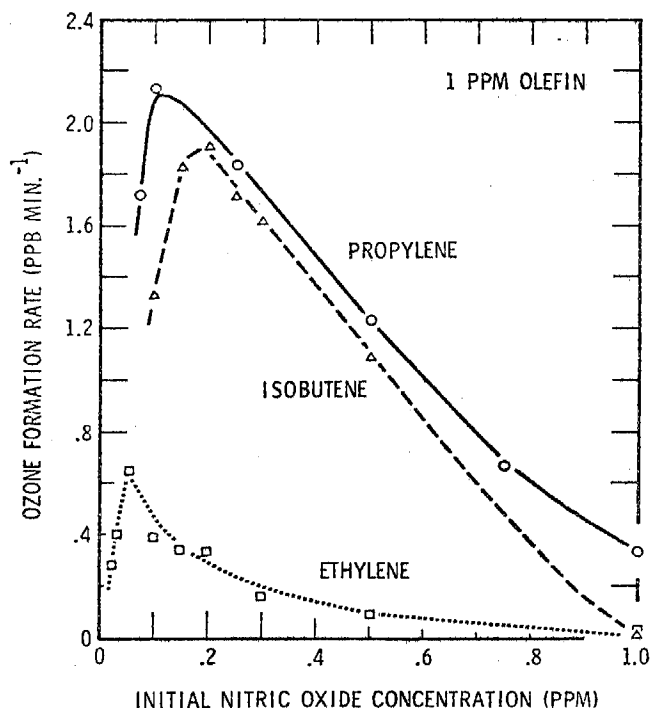
Figure 3. Nitric oxide inhibition of ozone formation (Glasson and Tuesday, 1970a)
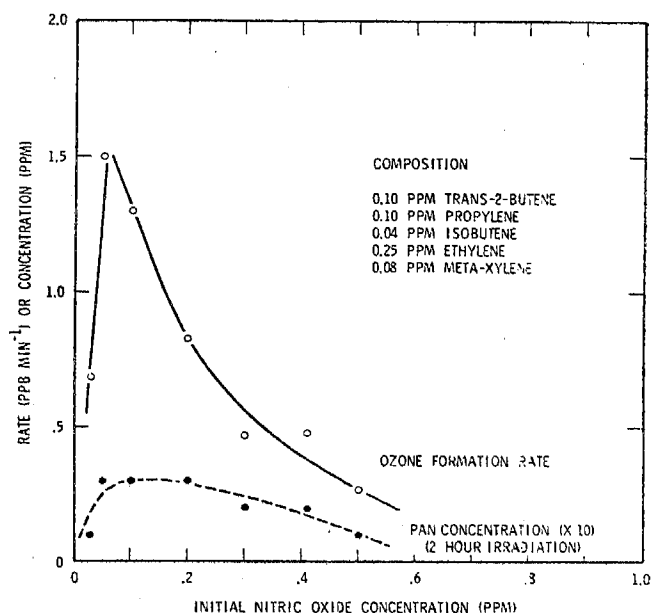
Figure 4. Nitric oxide inhibition of the atmospheric photo-oxidation of hydrocarbon (Glasson and Tuesday, 1970a)

A chamber study by Romanovsky and co-workers (1967) used three types of initial hydrocarbon:propylene, a mixture of hydrocarbons designed to simulate exhaust and authentic exhaust. The published discussion centers on the propylene results but a statistical analysis of the smog symptoms produced by each of the HC systems indicated fair agreement among the results of the three systems employed. Initial concentrations were quite high and thus this study is not applicable to the current problem.

Recent studies at the Bureau of Mines Laboratories (Dimitriades, 1972, 1970) is an example of a useful empirical auto exhaust study. An earlier study by Korth et al. (1964) is less significant because current GLC methods for detailed chemical characterization of the exhaust were not available and the concentration range covered does not extend to sufficiently low concentrations. The Bureau of Mines study was conducted in a systematic manner with considerable precautions against errors (Dimitriades, 1967). The total oxidant data obtained are summarized in a series of graphs, as 6-hour dosage vs. ppmC of hydrocarbon at constant NO_x in a report (Dimitriades, 1970) and as the interval within 6 hours for which oxidant exceeded 0.1 ppm for the same independent variables in a paper (Dimitriades, 1972).

Analysis of these data in terms of the California Standard of 0.1 ppm oxidant for one hour or less led to an empirical discriminant function (see Figure 5) having two branches passing through zero concentrations implying two regions of hydrocarbon-nitrogen-oxides concentrations capable of satisfying the standard. This result implies two ways to go for oxidant control, (1) drastic NO_x control, or (2) joint control of both NO_x and hydrocarbons, hydrocarbon control being the more severe (the present direction of California's control efforts).

There is no doubt that the discriminant function does have two branches, but there is considerable uncertainty associated with the position of the lower branch (Figure 5, line bc) since it was based, not on experimental data, but on the assumption that at sufficiently low NO_x concentrations oxidant decreases with decreasing NO_x concentrations (see Figure 6). As indicated
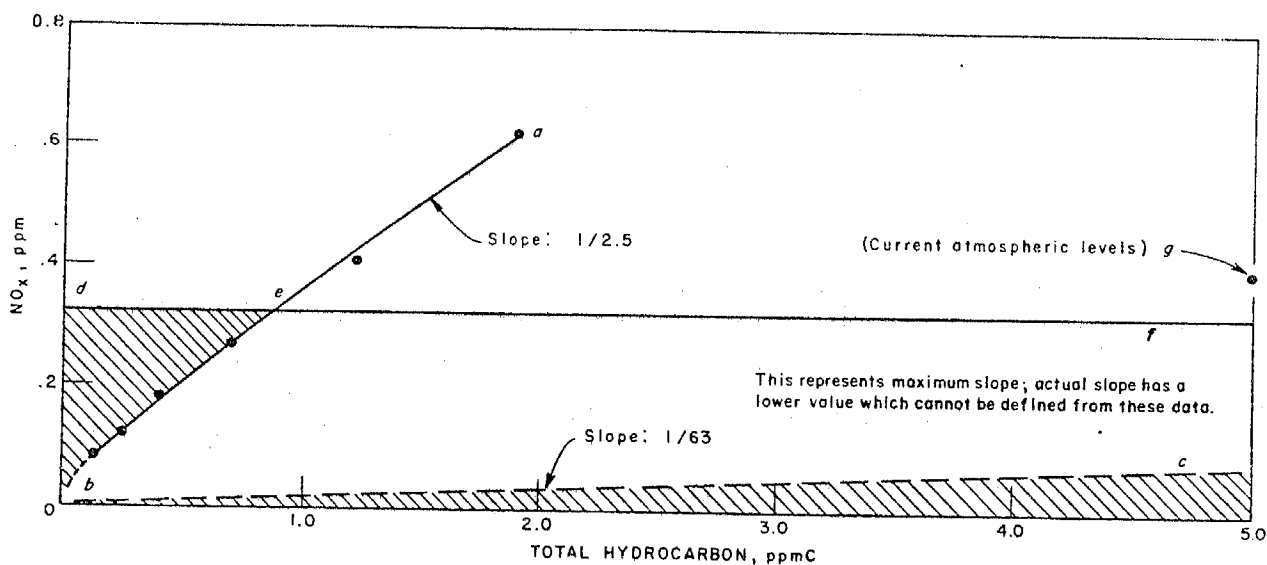

Figure 5. Equal response lines representing combinations of total hydrocarbon and NO_x corresponding to oxidant and NO_2 yields equal to the California Standards. Shaded area represents all points in the (HC, NO_x) plane that meet the California oxidant and NO_2 standards of air quality. (Dimitriades, 1970)
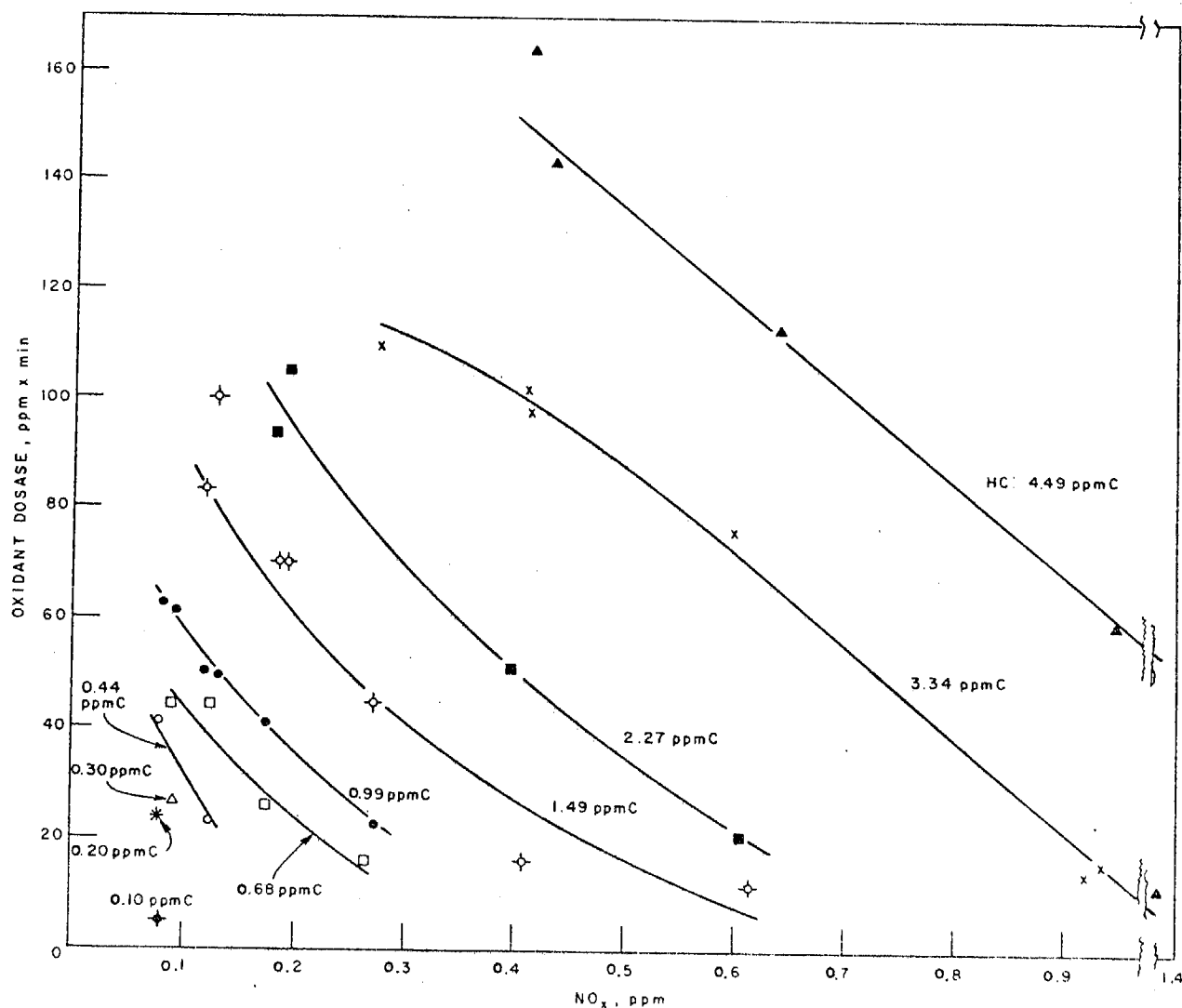
Figure 6. Oxidant-dosage reactivity of exhaust as a function
of NO_x at various HC levels (Dimitriades, 1970)

earlier, studies of the reactivity of single hydrocarbons or simple hydrocarbon mixtures (see Figures 3 and 4) do, in fact, show such a decrease in oxidant with decreasing NO_x, at very low NO_x concentrations. Dimitriades has noted from these data that the "oxidant maximum occurs at lower NO_x levels for less reactive HC:NO_x systems. Such oxidant maxima may, therefore, also exist in the exhaust system, but they occur at NO_x levels lower than those used in this study."

The Bureau of Mines data indicated that present ARB efforts toward oxidant control by appropriate reduction in both HC and NO_x, is perhaps the more correct course to follow. However, Dimitriades (1972) points out that the strict applicability of these data to the selection of the most appropriate control strategy is subject to the following assumptions:

(1) The hydrocarbon composition of exhaust is the same as that in the atmosphere.

(2) A change in the HC/NO_x ratio in the atmosphere is not accompanied by a change in the HC distribution (i.e., relative amounts of olefins, aromatics, and paraffins).

(3) The interdependence of initial reactants and resultant smog levels are the same in the smog chamber as in the air.

The most confining of these restraints is the second: the requirement of constant chemical composition of emissions. This study clearly indicates the need for more work on oxidant dependence in the region of low concentrations and on varying composition of the orgnic burden.

Some evaluation of the significance of these assumptions has been made in the current literature. For example, Dimitriades has dealt with each of these assumptions. Briefly his conclusions are as follows:

(1) Exhaust hydrocarbon composition differs from that of the atmosphere in lacking methane, ethane, propane and some additional amounts of higher paraffins thought to originate from gasoline evaporation. The first three are claimed to be of zero reactivity under ordinary HC:NO_x ratios; the higher paraffins have a reactivity similar to that of exhaust.

(2) The effect of HC:NO_x ratio on the chemical composition of HC will depend on the control method(s) used. Current hydrocarbon control methods do not seem to affect the distribution of HC but catalytic NO_x control has been found to preferentially remove the reactive hydrocarbons.

(3) Comparisons of smog chamber data with atmospheric results are not easily made but a single comparison using atmospheric data of Stephens and Burleson (1969) showed reasonable agreement for oxidant and PAN levels (see Table 1).

Table 1. Comparison of Smog Levels from an Atmospheric Sample and a Chamber Sample that Contain the Same Initial Reactant Levels (Dimitriades, 1972)

Sample	Initial reactant levels		Smog levels	
	Total nonmethane hydrocarbon, ppmC	NO_x, ppm	Oxidant, ppm	PAN, ppm
Atmosphere (Riverside, Calif., 10/24/68)........................	3.05	0.30	–	–
At 16:10 PST....................	–	–	0.40	0.034
Smog chamber.......................	3.13	.27	–	–
After 2-hr irradiation.........	–	–	.26	.034
After 4-hr irradiation.........	–	–	.49	.047
After 6-hr irradiation.........	–	–	.49	.044

Altshuller and Bufalini (1971) have delineated areas pertinent to smog chamber studies where the effects of variables associated with the formation of photochemical smog are not clearly established.

(1) A variety of contradictory results have been obtained for the effects of water vapor on hydrocarbon photooxidation; for example: increases-decreases or no effect on oxidant formation, and increases or no effects on rate of NO_2 formation, have all been reported. Resolution of these other discrepancies may be assisted by experimentally determining the role of surface effects and the importance of the $N_2O_5 + H_2O$ reaction in effecting a change in the $HC:NO_x$ ratio.

(2) The measurement of light intensity between 300 and 400 nm using the photolysis of NO_2 (k_d) favors the longer wavelength region because of the greater absorption coefficient of NO_2 in this region. Two sources for error must be kept in mind when using this method: (a) change in energy distribution of light source, and (b) the presence of compounds able to absorb light in the short wavelength region, e.g., aldehydes.

(3) The poor nitrogen balance observed for many $HC-NO_x$ irradiations may be accounted for, in part at least, by nitric acid possibly formed from hydrolysis of N_2O_5 or from $OH + NO_2$.

Analysis of Air Quality Data

Although much significant information has been acquired from the analysis of air quality data, the power of this technique cannot be fully utilized until sufficient air monitoring locations are available which measure a minimum number of key pollutants, e.g., total oxidant, NO_x, NO_2, total hydrocarbons, total non-methane hydrocarbons, and CO. In the future ambient levels specifically of ozone also should be determined. Of course, until this situation is rectified, maximum use will be made of the available data.

It is our understanding that the ARB has been compiling the data obtained by monitoring stations in most areas of the South Coast Air Basin. However, more work has to be carried out on data collected in some areas (e.g., the Riverside APC) to reduce the available information to the suitable forms for an appropriate computer analysis, e.g., reduction of data from strip charts so that they may be stored on computer tapes.

Analysis of air quality data has been undertaken by Federal, State and local agencies as well as by certain industries and Universities, including the SAPRC. Certain of these are collected on a continual basis, e.g., by state and local controlled agencies. It is not possible to tabulate all these previous analyses of air quality data since few are directly applicable to the approach being used here. However, the extensive statistical analysis of the CAMP Continuous Air Monitoring Project air quality data by Larsen (1967, 1971) should be mentioned. By utilizing data acquired at various locations in the country including downtown Los Angeles, he found that pollutant concentrations appeared to fit a general mathematical model with the following characteristics:

1. "Pollutant concentrations are lognormally distributed for all averaging times."

2. "Median concentrations are proportional to averaging time raised to an exponent."

3. "Maximum concentrations are approximately inversely proportional to averaging time raised to an exponent."

Computer Models of Photochemical Smog Formation

In discussing models for photochemical smog, it is important to recognize that there is a significant difference among the various computer models and the way in which they are used. The SAPRC has recently submitted a substantial proposal to NSF-RANN which contains a significant section on model development entitled "Utilization of SAPRC chamber data to develop an experimentally validated computer model and its application to real atmospheres." Although this is a two-year program with a proposed starting date of October 1, 1973, there will be significant benefit to the ARB from the proposed NSF study, since a coordinated program is being developed at the SAPRC to address critical questions such as those posed in this current ARB proposal. Although the objective of this ARB proposal is to develop a more limited model than for NSF-RANN, i.e., relating the function of the $HC:NO_x$ ratio to oxidant formation, the ARB will benefit from the more exhaustive modeling work to be performed by the SAPRC under NSF funding.

It is pertinent here to use extracts from the NSF-RANN proposal concerning the background on the various modeling studies; this avoids needless duplication of time and effort.

"The most general model is an empirical one based on past air quality data and meteorological input to predict the likely pollutant level, e.g., oxidant, which is the pollutant of major concern in the California South Coast Air Basin. This type of approach has been used by Schuck, Pitts and Wan (1966) and brief details are given in the background section. Additionally, Dr. Behar of the SAPRC developed a set of computer maps showing oxidant build-up during a typical summer day in the South Coast Air Basin. (Behar, 1972)"

"Going a step further in sophistication, a general, relatively simple chemical kinetic model is utilized in conjunction with a meteorological, source, and a dispersion model in the development of an airshed model. Due to limited finances, computation time is finite and hence the chemistry model of necessity involves less than about 20 reactions. Among the workers in this area are Eschenroeder at General Research Corporation, Roth at Systems Applications, Inc., Wayne at Pacific Environmental Systems, and Sklarew at EPA (formerly at Systems, Science and Software)." (These studies have been discussed in recent reviews: "Simulation of Urban Air Pollution" by Seinfeld, Reynolds, and Roth (1972) and "Concepts and Applications of Photochemical Smog Models" by Eschenroeder and Martinez (1972))

"Lastly, one has a very detailed kinetic model which has about 100 or more chemical reactions. The model is developed by fitting computed concentration-

time profiles of key species such as ozone, nitric oxide, nitrogen dioxide, hydrocarbon, etc., with experimental profiles obtained from smog chamber studies. It is evident that the more accurate and more numerous the experimental profiles, the better will be the chemical model. With our new and unique smog chamber facility to supply the experimental data, it is the latter type of modeling approach that we intend to follow initially. This approach has recently been employed by Calvert, Demerjian and Kerr (1972), Niki, Daby and Weinstock (1972) and Hecht and Seinfeld (1972). Key earlier work was reported by Westberg and Cohen (1969) and Wayne and Ernest (1969)."

C. Overall Objectives

Control of NO_x in emissions from motor vehicles in California has been underway since 1971 (1973 nationally) while reduction of hydrocarbons has been in effect since 1966 in California (1968 nationally). Federal implementation plans, however, determine anticipated oxidant reduction solely on the basis of the reduction in hydrocarbons and do not include oxides of nitrogen. These implementation programs are being carried out despite the fact that the interrelationship between oxidant levels and hydrocarbon and nitrogen oxide levels are uncertain, especially at realistically low levels of nitrogen oxides and hydrocarbon. It is in this region that present chamber data are either nonexistent or unreliable. Furthermore, chamber oxidant data are more strongly influenced by the nature of a particular chamber.

It is in part for these reasons that the rationale for setting Federal standards for hydrocarbons and oxidant are based on atmospheric observations rather than chamber data. However, this appeal solely to the "real world" critically involves the questionable hypothesis that fluctuations of present day polluted atmospheres toward conditions producing low oxidant can represent a controlled atmosphere of the future.

If this hypothesis is regarded as dubious then there is no alternative but to additionally include the use of new chamber data in the development of implementation plans. Of course, this will include use of experimentally validated chemical models which depend heavily on reliable chamber data. Such models will eliminate some of the empiricism currently involved in chamber data interpretation. Since much available data on oxidant in chambers from photooxidations at low concentrations are suspect new data will have to be obtained under circumstances which eliminate or suppress the factors which contribute to uncertainty of the data.

In addressing the pertinent and necessarily demanding tasks set for the SAPRC by the ARB, we must make maximum use of all existing relevant data. As indicated earlier, included in this category are the air quality data for the South Coast Air Basin.

It is common knowledge that emission control systems installed after 1965 on automobiles in California had the effect of reducing hydrocarbons and carbon carbon monoxide, while increasing emissions of nitrogen oxides. Thus, a crude

experiment of the desired type, namely determination of oxidant level dependence on variation in hydrocarbon and NO_x concentrations, has already been carried out in the real atmosphere. The effect on air quality has been documented through the recorded values of oxidant, NO_x, etc., by monitoring stations at selected locations throughout the South Coast Air Basin. The effect of this control strategy on air quality at various locations throughout the basin may be analyzed from these data plus an emissions inventory of hydrocarbons and nitrogen oxides for the same period. Although it is recognized that the type of information gained from an analysis of the air quality data from about 1960 to the present will be qualitative, it should be one of the tools used in elucidating the effect of reducing either hydrocarbons or both hydrocarbons and NO_x in improving air quality.

A combination of analyses of newly obtained chamber data as well as ambient air monitoring data should result in the development of an experimentally validated chemical "model" for the dependence of both oxidant and specific ozone formation on levels of hydrocarbons and oxides of nitrogen. This model and the refined chamber data could then be used to assess the magnitude of reduction in hydrocarbons and possibly NO_x which will be necessary to achieve the ambient air quality standard for oxidant.

A final objective is to obtain information concerning the effects of "yesterday's smog" on "today's emission burden." To our knowledge there is a distressing lack of data relevant to this question. However, we feel it is one which is amenable to scrutiny using our SAPRC chamber facility.

D. Specific Aims

1. To develop a validated simulated smog mixture which will serve as the primary sample in the smog chamber studies. This mixture will be representative of the early morning Los Angeles atmosphere, but will be validated against the behavior of both auto exhaust and Riverside ambient atmospheres.

2. To further characterize as needed for the SAPRC-ARB 1973-1974 program the properties and operational characteristics of the SAPRC chamber facility.

3. To define in the systems to be studied the relationship between levels of total photochemical oxidant vs. the specific level of ozone . . . the major health hazard.

4. To evaluate, and then test experimentally, the validity of certain aspects of key previous work, particularly that of Dimitriades, Altshuller and co-workers, Hamming and co-workers, and Tuesday et al.

5. To extend the "high concentration" studies of other workers into the "low concentration" regime applicable to forecasted ambient atmospheres in the latter part of the 1970's. This will be based on reductions expected from present or proposed implementation strategies (e.g., across-the-board reduction).

6. To determine the impact of oxygenates, PAN's and NO_2, (i.e., remnants of "yesterday's smog"), as well as actual aged smog, on morning ambient air ("today's smog") samples photolyzed in the SAPRC chambers.

7. To analyze existing air monitoring data (e.g., LAAPCD data) to determine empirically the effects on oxidant levels of control strategies which have been implemented to date, and to use results from these analyses in the design of additional relevant experiments to be performed in the SAPRC chamber facility.

8. Utilizing the data and results obtained in 1-7, we will insofar as possible define in terms of a reliable and operationally useful model the functional dependence of the concentrations of ozone and total oxidant on those of hydrocarbons and oxides of nitrogen at present ambient levels and then in the low concentration regime. The HC/NO_x/ozone-oxidant model will be programmed so as to be directly applicable to the questions posed to the SAPRC by the ARB.

E. Technical Plan (Methods of Procedure)

The technical plan is broken down into three parts concerning: (a) analysis of both existing air quality data and past chamber data; (b) an experimental program conducted in the SAPRC chamber laboratory; (c) generation of a chemical model for the HC/NO$_x$/O$_3$ system which will be applicable to both simulated and real atmospheres. The specific methods of procedures to be employed in the general parts of these tasks are cited below (not necessarily in the order of execution).

1. Development of a Smog Surrogate for Experimental Chamber Studies

In developing the research program presented in this proposal we have been confronted by a fundamental decision concerning the nature of the basic test sample to be used in conducting the HC/NO$_x$ study. This decision involves the choice between (1) employing diluted automobile exhaust, or (2) a simulated atmospheric mix corresponding to say the L.A. early morning traffic peak, and (3) real Riverside ambient air. Generally, only the first two kinds of "control" samples have been employed in previous chamber experiments. Each of the three approaches has its own advantages and limitations.

We choose to base our experimental chamber program on a synthetic multicomponent system which is currently being developed in the SAPRC chamber facility under our present ARB contract. In this contract renewal, we propose to expand our efforts in the development of this mix by testing its capacity to mimic the smog manifestations of (a) photolysed dilute exhaust to be obtained from the ARB El Monte Laboratory, and (b) early morning Riverside ambient air photolysed in the SAPRC chambers. By choosing to use a simulated atmospheric mix we will avoid the difficulties and limitations of dilute exhaust studies such as irreproducible starting compositions and contamination of the chambers (which would considerably nullify one of the principal strengths of the SAPRC facility, i.e., ability to maintain clean chamber operating conditions).

One of the major assumptions associated with the use of auto exhaust to simulate polluted ambient air in smog chamber studies is that the hydrocarbon distribution is sufficiently close to that of the atmosphere to allow the essentially same chemistry to occur. In particular the C$_1$ - C$_3$ paraffins are considered unreactive and their presence in the atmosphere should not affect the chemistry significantly. This is probably a reasonable assumption at current ambient hydrocarbon levels but may not be at the lower ambient levels resulting from present and future implementation plans. Stephens (1971) has suggested from his studies with ambient air samples that all classes of hydrocarbons contribute to the conversion of NO to NO$_2$. "The lower reactivity of paraffins as compared to olefins and aromatics is offset at least partially by their presence in larger amounts."

Stephens and Burleson (1969) in a detailed analysis of hydrocarbons in ambient air has found that the hydrocarbon distribution resembled that of auto exhaust except for the presence of much larger amounts of C$_2$ through C$_5$ paraffins. This excess of lower paraffins in part can be accounted for by natural gas (methane and C$_2$) and gasoline vapor (C$_3$ - C$_5$).

As auto exhaust control strategies are implemented, the contribution of non-exhaust sources of the $C_2 - C_5$ paraffins becomes increasingly important.*

A quantitative estimate of the contribution of $C_2 - C_5$ paraffins in photochemical smog reactions has been made by Stephens and Burleson (1969), (see Tables 2 and 3). More than 25% of the hydrocarbons reacting are $C_2 - C_5$ paraffins. The contribution of C_2 and C_3 is about 1.5% of the total. These estimates have been confirmed by actual irradiation (6 hours) of samples of early morning ambient air containing comparable amounts of hydrocarbons (Stephens and Burleson, unpublished results).

The major criticism of the use of synthetic mixtures as opposed to exhaust has been that <u>simple</u> HC:NO_x mixture are unrealistic and fail to quantitatively reproduce smog manifestations demonstrated by irradiated dilute exhaust. However, even workers who have employed exhaust concede as Dimitriades (1972) says "that exhaust behavior can probably be simulated in synthetic mixtures if such mixtures are carefully designed and tested by direct comparison to exhaust at various HC:NO_x ratios."

We propose to employ a mixture designed to simulate the early morning Los Angeles atmosphere mix such as that given in Table 4, and to test this mixture against exhaust samples to be furnished by the ARB as well as against actual ambient air at the SAPRC.

<u>Table 4</u>. Simulated early morning Los Angeles atmospheric mix.

Compounds	ppbC
m–Xylene	326
Toluene	114
n–Butane	782
2,3 Dimethylbutane	615
cis-2-butene	62
2-Methyl-2-butene	70
Ethene	84
Propene	35
Acetylene	101
Methane	2800
Ethane	160
Propane	40

The test of authenticity will consist of monitoring the correspondence in behavior of at least the following ten smog manifestations or variables:

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*This argument can be applied to stationary sources as well. The EPA control strategy plan for 1977 would reduce mobile source hydrocarbon emissions from 70% to 26%, thus increasing emissions from stationary sources from 20% to 40% of the total.

Table 2. Estimate of amounts reacted in an ambient air sample compared to an unreacted sample.

	Reacted Sample (ppb) 1610 PST 10/24/68		Unreacted Sample (ppb) 0730 PST 9/24/68
	Present	Reacted (Δ)	Present
Methane	2530	0	2355
Ethane	72.2	0.6	63.6
Propane	49.9	2.6	18.8
[C]Acetylene	42.0	6.3	77.0
Ethene	17.9	23.1	65.6
Propene	1.27	10.7	19.2
Methyl Acetylene	1.2	0.3	2.6
1,3-Butadiene	0.29	1.5	3.6
[O]1-Butene	0.26	2.3	2.6
Isobutene	2.0	3.2	5.2
Trans-2-Butene	<0.2	1.4	1.4
Cis-2-Butene	<0.2	1.4	1.4
2-Methyl Butene-1	0.35	2.1	2.4
Cyclo Pentene[a]	0.8	3.2	4.4
Trans-2-Pentene	<0.2	2.4	2.4
2-Methyl Butene-2	<0.2	2.6	2.6
[P]Isobutane	19.7	3.0	8.0
N-butane	62.0	16.3	27.6
Isopentane	41.2	12.8	39.2
N-Pentane[b]	21.4	7.9	22.4
Cyclo Pentane	2.4	0.6	3.2
2,2-Dimethyl Butane[c]	0.86	0.3	1.6
2,3-Dimethyl Butane	1.9		3.8
2-Methyl Pentane[d]	9.6	4.4	12.4
3-Methyl Pentane	6.1	3.9	8.4
N-hexane	8.3	3.5	9.0

Includes: [a] 2-Methyl Butadiene-1,3; [b] 3-Methyl Butene-1; [c] 1-Pentene; [d] Cis-2-Pentene.
C, O, P—See Table V

Table 3. Riverside ambient air (ppb) on roof of health-finance building. 1610 PST 10/24/68 (In ppb by volume except where noted.)

Compound	Present	+	Reacted[a]	=	Initial[a]
C1 - C3 Paraffins (meas.)	2652		3.2		2655
Non-fuel unsaturated[C] (meas.)	62.7		41.9		104.6
C4 - C5 Olefins[O] (meas.)	3.4		18.6		22.0
C4 - C5 Paraffins[P] (meas.)	173.5		52.7		226.2
Higher olefins (est.)	2.2		19.6		21.8
Higher saturates (est.)	42		21.0		63.0
Aromatics (est.)	67		40.9		107.9
Total (less CH4)	473		198		671
Total (ppbC, incl CH4, GLC)	4800				
Total (ppbC, non GLC)	6000				
Acetylene	42.0				48.3
Carbon monoxide	5000				
Oxidant	400				
Nitrogen oxides	60				300
PAN	34				

[a] estimated
C, O, P—See Table IV

NO, NO_2, O_3, total oxidant, PAN, formaldehyde, CO, individual hydrocarbons (C_1 through C_6 plus oxygenates and aromatics), total hydrocarbon, and "aerosol" (opacity).

2. Capabilities and Methods of Operation of the SAPRC Chamber Facility

A detailed description of the operational characteristics and methods of use of the evacuable and glass chambers, the in-situ longpath infrared spectrophotometer, and the solar simulator is given in Section II.B - Existing Facilities

3. Characterization of the Properties of the SAPRC Chambers and Solar Simulator and Sample Measurements

The success of the proposed chamber program will depend critically on our ability to characterize the behavior of the SAPRC facility and the samples employed. Fortunately, the major portion of the concurrent EPA chamber program consists of experiments which will determine the chemical and physical characteristics of the evacuable chamber and solar simulator. For example, such properties as ozone decay (both light and dark), leak rate, spatial uniformity, and absolute intensity of photolysing radiation, sample homogeneity, surface effects, rates of thermal oxidation of NO, and effects of variations in CO concentration will all be investigated under the EPA program. In addition, standard CAPI-6 experiments (O_3 light and dark decay, leak rate, NO-propylene photolysis) will have been conducted in the glass chamber a number of times prior to the start of proposed research so that this chamber will also be well characterized.

A large number of physical and chemical properties will be measured during runs. These are tabulated in Table 5 along with the concentration range of applicability, method of analysis, and estimates of precision and accuracy.

All analytical instruments will be periodically recalibrated to establish their stability and analytical data will be recorded in a standardized format which will include precise designation of all sampling times. In addition to tabulation of times and concentrations, data will be plotted in graphical form for each variable. Error limits will be calculated and stated for each measurement made.

4. The Relationship Between Total Oxidant Values and Actual Levels of Ozone and Nitrogen Dioxide in Ambient Air

For a variety of chemical, biological, and medical reasons, it must be recognized that an oxidant value does not necessarily correspond to the actual level of ozone in ambient air. "Total oxidant" represents those compounds present in ambient air which oxidize potassium iodide to give free iodine. It generally consists primarily of ozone, but it also includes such compounds as nitrogen dioxide and peroxyacetyl nitrate, both of which also oxidize potassium iodide solution. The efficiency of this oxidation varies from compound to compound, but for three key components of photochemical oxidant, it is 100% for ozone and approximately 15 to 20% for both nitrogen dioxide and PAN. The following points should be noted:

Table 5. Physical and Chemical Parameters to be Measured

Parameter	Range	Method	Precision	Accuracy
Total HC	0-10 ppm	GC	± ½% F.S. or 0.05 ppm, whichever is greater	Limited by Calibration Standard Typically ± 1%
Individual HC's	0.5-1 ppb 1-2 ppb >2 ppb	GC GC GC	± 15% ± 10% ± 2%	Limited by Calibration Standard Typically ± 2%
Ozone	0-20 ppm	Dasibi O_3 Analyzer	± 1% F.S.	± 3%
Total Oxidant	0-1 ppm	Mast Analyzer	± .05 ppm	± .05 ppm
NO NO_2 NO_x	0-5 ppm 0-5 ppm 0-5 ppm	Chemiluminescent Analyzer	± 2% F.S. By difference ± 2% F.S.	± 5% By difference ± 5%
PAN	>50 ppb	LPIR	± 20%	± 20%
Formaldehyde	>10 ppb	LPIR	± 20%	Limited by Calibration Standard
Acetaldehyde	>100 ppb 1.5-3 ppb 3-6 ppb 6 ppb	LPIR GC GC GC	± 20% ± 15% ± 10% ± 2%	Limited by Calibration Standard Limited by Calibration Standard Limited by Calibration Standard Limited by Calibration Standard

Table 5. (continued)

Parameter	Range	Method	Precision	Accuracy
CO	0-10 ppm	GC	$\pm \frac{1}{2}\%$ F.S. or .05 ppm, whichever is greater	Limited by Calibration Standard Typically $\pm$ 1%
Chamber Pressure	0-800 torr	Validyne Gauge	$\pm$ 10%	10%
Temperature	-40 to +100° C	TC	$\pm$ 0.5° C	0.5° C
Time of Dilution	...	Clock reading	$\pm$ 10 sec	...
Light Intensity	0-1 Solar Constant	Spectroradiometer	To be determined	To be determined
Relative Humidity	0-100%	Dewpoint Apparatus or Hygrometer	$\pm$ 2% R.H.	$\pm$ 2%

a) PAN levels on smoggy days generally fall in the 5 to 50 ppb range. These levels are so low in relation to ambient O_3 and NO_x that they do not significantly affect the observed total oxidant value.

b) NO_2 levels can approach those of ozone (although generally not concurrently). Thus, in an extreme case, if one has 0.5 ppm of NO_2 in ambient air (a high, but not impossible, level), one will see a total oxidant reading approximating the air quality standard for oxidant--0.08 ppm--yet no ozone is present! The ramifications of these facts are clear. All of the compounds contributing to a "total oxidant" must be measured individually and quantitatively.

A major disadvantage of using total oxidant readings as the only measure of oxidants (other than NO_2) is the inability to determine the presence of some unidentified oxidant (e.g., HOOH, ROOH, HNO_3) which may become important only under certain conditions. Measurement of total oxidant, ozone, PAN and NO_2 for all experiments should resolve this.

A final problem is determining oxidants which are not measured by the total oxidant monitor. For example, Dimitriades (1972) reports up to 0.15 ppm of N_2O_5 in his chamber experiments under certain conditions. This is not measured as part of total oxidant due to almost complete loss in the sampling line. However, in our facility formation of N_2O_5 can be monitored in evacuable chamber experiments by means of the completely non-destructive in-situ longpath infrared spectrophotometer.

5. $HC/NO_x/O_3$ Experiments

Utilizing the simulated atmospheric sample and the well characterized chamber facilities described above, a systematic study of ozone and oxidant dosage as a function of NO_x at various HC levels will be undertaken in the concentration regime (0.1-1.0 ppm NO_x; 0.2-5.0 ppmC HC) employed by previous workers. (Dimitriades; Hamming) Careful comparison of previous results with our own will be made by sufficiently sophisticated statistical analyses. As many as a dozen chamber runs may be employed to establish our relationship to previous work.

We will then extend these experiments into the critical concentration regime (<0.1 ppm NO_x; <0.5 ppmC HC; ozone/dosage <50 ppmC x min) where great uncertainty exists concerning the functional relationship between ozone, oxidant, HC and NO_x, and yet which represent just those levels toward which present day atmospheres presumably will evolve under the effects of present and future control strategies. The bulk of our chamber runs then will be devoted to a set of factorial design experiments in which initial reactant levels of HC, and NO_x are chosen so as to vary systematically from low to high values (within the indicated concentration ranges) for perhaps five different HC/NO_x ratios.

6. Investigation of Effects of "Aged Smog" on Photochemical Air Pollution

Due to the almost complete lack of information concerning effects of "yesterday's" smog it is possible to conceive of a number of straightforward and yet highly relevant experiments which will yield new data about this question.

a.   The simulated atmospheric sample developed as described above will be photolyzed under a standard set of conditions for eight hours. It will then be permitted to remain undisturbed in the chamber overnight. The following morning the same standard sample will be introduced into the "aged" chamber contents and a second photolysis will be made.

b.   A second kind of experiment, suggested by Mr. Hutchison, ARB Chief of Research, will involve injecting a sample representative of the morning emission burden into ambient air obtained in the early morning hours, i.e., prior to sunrise and to traffic buildup. This system would then be photolysed for 6-8 hours and the resultant smog manifestations compared quantitatively to those for the case of the emission sample injected into a pure air matrix followed by photolysis.

Considerable effort would have to be made to insure that representative samples of ambient air are employed. In particular the nature of ambient air samples obtained as a function of altitude in the vicinity of the laboratory would be of considerable interest. We have been assured that the Air Resources Board will lend full cooperation in obtaining information of this type including the possible use of an instrumented aircraft. Samples could then be obtained simultaneously at ground level and at various altitudes above the laboratory site. An additional possibility is to build a guyed sampling tube, say 100 feet in height, with inlets spaced along its length. It could be so designed that an average sample is obtained over the 100-foot range above the SAPRC roof.

c.   A third experiment which might be of interest would be to inject known quantities of those species which are expected to be relatively stable overnight, i.e., PAN, NO_2, oxygenates into the standard morning-atmosphere simulation sample and observe differences under photolysis from a sample irradiated without injection of such smog "remnants."

7. Analysis of Existing Data

This task can be considered under three major categories.

a.   In addition to our present data bank at the SAPRC, additional available air quality data for the South Coast Air Basin will be acquired from the Air Resources Board in a form suitable for manipulation by the computer at UC Riverside. These data will be analyzed in terms of the variation of oxidant levels, both before and after the introduction of emission controls on post 1965 motor vehicles. Included in the analysis will be the peak oxidant readings, frequency of exceeding the Federal air quality standard for oxidant of 0.08 ppm for 1 hour and also the total dosage.

A statistical analysis of the data will also be undertaken following the approach used by Larsen (1971).

b.   In examining control measures for emissions of hydrocarbons and NO_x, it is important to take a realistic look at processes occurring in the real atmosphere. Included in this is an examination of the effect of emissions of pollutants from both mobile and stationary sources into the atmosphere during non-sunlight hours. It appears unrealistic to completely neglect the effect

of these emissions on air quality and oxidant production. It has been suggested (Johnston, 1970) that nitrous acid may be formed during the night to provide a ready source of the highly reactive hydroxyl radical as soon as the sun rises.

A recent finding of the joint UCR-NASA airborne monitoring program suggests that indeed this aspect of the pollution problem needs further exploration: a flight measurement in March 1973 carried out in the Los Angeles Basin before the sun arose, detected significant ozone levels (~ 0.06 ppm) at about 2000 feet whereas the ground level readings were approximately zero. Of course, this phenomenon may be due to a reduction of the background levels of O_3 due to the nighttime emissions of NO. However, this is just one possible explanation. Clearly, if we are to address the critical questions posed by the ARB, including the effect of today's emissions on yesterday's smog, this finding should be further explored and the results utilized for our investigation of the $HC/NO_x/$ oxidant function.

c. The third aspect of this particular work task of the proposal is to maximize the utility of not only previous analyses of air quality data but also relevant smog chamber studies. The critical analysis of smog chamber studies is a very necessary function to examine the reliability of results of previous chamber studies and their applicability to the real atmosphere, e.g., the analytical methods of some past chamber studies are very questionable; the representation of real ambient air and exhaust by synthetic mixtures in a significant number of past studies has been very unrealistic. (This aspect was mentioned in the discussions above under the "Background" Section.)

It is imperative that our knowledge is built on reliable data to form a firm base in focusing on the key questions to be addressed in this proposal. Thus, all data of questionable reliability should be rejected and permanently "labeled" as such.

In conclusion, the basis for relating the control of oxidant to studies on eye irritation observed for various hydrocarbon: NO_x ratios will be examined: it is quite possible that eye irritation may remain unaltered while the oxidant concentration changes.

8. Development of a Model of the Relationship Between $HC:NO_x$ Ratios and Ozone-Oxidant Formation

One of the key thrusts of this program is the development of a model which accurately predicts the dependence of oxidant and ozone formation on $HC:NO_x$ ratios. In order to obtain such a model, major reliance will be placed on data developed in the chamber program. This will be supplemented by relevant information obtained for the technology assessment section of the proposal.

Specifically, results of chamber studies using both ambient air and surrogate mixtures (in which the effect of varying the $HC:NO_x$ ratio on oxidant formation will be explored) and carried out under realistic conditions will be utilized to elucidate the critical parameters which affect the relationship of $HC:NO_x$ and oxidant. Such parameters may include those currently recognized, such as the composition and reactivity of the hydrocarbon mix. However, basic information generated on programs funded by other agencies, on such facets as ozone-

olefin reactions and processes involving the highly reactive hydroxyl radical will be utilized and incorporated into the current proposal to provide an additional input. In addition, the sophisticated instrumentation associated with the chamber may reveal other compounds or intermediates which critically affect oxidant formation under certain conditions of HC and NO_x concentrations.

Thus, a combination of both basic (funded by the NSF) and applied research (funded by the ARB, EPA and hopefully NSF-RANN) will be utilized to explore the dependency of oxidant on NO_x and HC. A more detailed discussion of the exact mechanism of how information will be merged from these different sources into a model will have to await the generation of results from the actual program and the mini-conference being held this spring at the SAPRC to discuss the topics being addressed in this proposal.

F.   Schedule

The program proposed will begin with the further development and refinement of an experimentally validated simulated atmospheric sample based on work begun during the present ARB contract. We will then begin the HC/NO_x/ozone-oxidant studies, initially at concentrations comparable to those employed by previous workers and then at lower concentrations. These studies are expected to occupy the bulk of chamber runs during the first three quarters of the contract period. The aged smog studies involving ambient air samples will be conducted in the final quarter, i.e., during late spring and early summer when high pollutant levels occur.

The analysis of ambient air quality data and post chamber data will begin immediately at the start of the contract period and should continue for the duration of the contract as new monitoring and chamber data continue to become available.

Development of computing methods and programs for the HC/NO_x/ozone-oxidant modeling effort will begin at the start of the contract and be carried concurrently with the chamber experimental program during its twelve-month duration.

G. Some Preliminary Results from SAPRC Chamber Experiments

Initial efforts in the SAPRC facility have been devoted principally toward an understanding of the properties and operating characteristics of the two chambers and the solar simulator in its present configuration. Specifically, we have been engaged in: 1) characterization of the pure air system; 2) generation of initial information on the behavior of the glass chamber; 3) characterization of the evacuable chamber – 10 KW solar simulator combination.

1. Characterization of the pure air system

The operation of this key subsystem remains at the stage where it provides dry, unheated pure air to both chambers. Hydrocarbon analyses are obtained at the beginning of each chamber experiment. Typical of pure air analyses results obtained to date is the pair shown in Table 6. One analysis was obtained in the Glass Chamber immediately after charging, the other, reflects chamber off-gassing over a period of time.

The table reveals that under realistic conditions of dry air irradiation the initial levels of hydrocarbon are close to the design specifications, but substantial quantities of oxygenates off-gas from the glass chamber walls. This remains a persistent problem. Subsequent experiments have shown that operation of the sonic pumps substantially increases the levels of oxygenates and CO in the chamber. We suspect the driver cones in the sonic pump as a major contamination source and are taking steps to reduce off-gassing contamination in the glass chamber.

2. Behavior of the Glass Chamber

We now have performed the initial experiments designed to characterize the behavior of the glass chamber with respect to a) light intensity, b) oxidant formation upon irradiation of pure air, c) background reactivity with respect to propylene disappearance, d) reproducibility of data from irradiation of NO-propylene mixtures, e) leak rate, and f) ozone reactivity.

a. Our initial measurement of light intensity was obtained by measuring the NO_2 disappearance during photolysis of 2 ppm NO_2 in nitrogen.

We report here a preliminary value of K_d

$$K_d = \tfrac{1}{2} \ln \frac{(NO_2)_i}{(NO_2)_f} = 0.30 \text{ min}^{-1}$$

for blacklight irradiation. This measurement was made, however, under conditions of high initial NO (0.14 ppm) and will be repeated under more carefully controlled conditions. The presence of NO suggests that the K_d value given represents a lower limit to the true value.

b. Oxidant formation during irradiation of pure air.

Results to date indicate that oxidant forms to the extent of about 0.2 ppm, and that virtually all of the oxidant is ozone. Table 7 summarizes

Table 6. Hydrocarbons Present During Photolysis of Pure Air
Glass Chamber, January 17, 1973

Compound[1]	ppb, T = 0	ppb, T = 17 hrs.
Methane	606	680
Ethylene	2.4	4.6
Ethane	6.5	9.2
Acetylene[2]	3.8	3.8
Propane	1.8	2.4
Propylene	0.2	0.4
Isobutane	0.1	0.5
n-Butane	0.2	1.0
Acetylene[3]	6.0	5.4
Isopentane	0.0	0.6
n-Pentane 3-Methylbutene-1	0.0	0.0
Acetaldehyde	7.4	120
Propionaldehyde	4.8	14.3
Acetone	4.4	81.5
Methyl ethyl ketone	1.0	9.6
Toluene	0.8	7.6

(1) Other compounds analyzed for but not found were: 1-butene; isobutene; cis and trans-2-butenes; 3-butadiene; methyl chloride, methylacetylene; 2,2-dimethyl butane; 1-pentene; 2-methyl butene-1; cis and trans-2-pentene; 2,3-dimethyl butane; 2-methyl and 3-methyl-pentanes; 2-methyl butene-2; cyclopentane; cyclopentene; n-hexane; 2-methyl butadiene-1, 3: Benzene; α-pinene; β-pinene; ethylbenzene; p-xylene; m-xylene; isopropyl benzene; o-xylene; n-propyl benzene; p-ethyl toluene; m-ethyl toluene; styrene; o-ethyl toluene; 1,3,5-trimethyl benzene; 1,2,4-trimethyl benzene; 1,2,3-trimethyl benzene.

(2) Run on Poropak-N column.

(3) Run on DMS column.

the results.

Table 7. Pure Air Photolyses in Glass Chamber

Date	O_3, ppm		Oxidant, ppm	
	6 hrs.	max.	6 hrs.	max.
1/17-18	.065	.18	--	--
2/7	--	--	--	0.22
2/9	--	--	0.22	0.24

c. Background reactivity with respect to propylene disappearance.

A standard method of examining chambers for background reactivity is to photolyze about 1 ppm of propylene in air, monitoring oxidant and propylene concentrations. Results of our first experiment in the glass chamber are depicted in Figure 7. Initial NO_x levels were less than 5 ppb as measured by a chemiluminescent analyzer, and thus are not sufficient to account for the observed results. A preliminary data analysis by Dr. Doyle indicates that the direct photolysis of the ubiquitous oxygenates in the glass chamber can account quantitatively for these observations.

d. Photolysis of mixtures of NO and propylene are a common way of generating data on chamber reproducibility. The data of Figures 8 and 9 were generated using dry air as a matrix, rather than the 25% relative-humidity conditions specified by the Coordinating Research Council. This course was taken so that relative humidity effects may be examined systematically at a later date. The data obtained from Figures 8 and 9 are summarized in Table 8. The excellent agreement between the time-dependent behavior of variables in these two runs was very gratifying in view of difficulties encountered in obtaining reproducible results in early runs made in previous chamber facilities.

e. Chamber leak and flushing rates

Figure 10 depicts the behavior of the glass chamber during a typical flushing operation with pure air. Sufficient CO was injected to give an initial concentration of about 10 ppm, and the dilution was monitored for two different flushing rates. It is seen that the CO decay follows the expected semilogarthmic behavior until the concentration of CO in the pure air approaches that in the chamber, and that at a flushing rate of 11.5 CFM, we expect to replace about 90% of the chamber contents each hour.

We have now measured a worst-case chamber leak rate. The loss of CO was followed over 19 hours with the sonic pumps in operation. The results (Figure 11) show a leakage of 1.25% per hour. A subsequent measurement of ozone decay with the sonic pumps off, however, shows that under normal, static

1973 March 8-9
Glass Chamber
Propylene + Air
Backlight Irradiation

Propylene

O_3

ppb

Time, hrs.

I-28

Figure 7

Figure 8

1973 February 23
Glass Chamber
NO - 0.28 ppm
C_3H_6 - 0.52 ppm

Time, hrs.

Concentration, ppm

Figure 9

1973 March 5
Glass Chamber
NO - .225 ppm
C_3H_6 - .50 ppm

I-30

Time, hrs.

Concentration, ppm
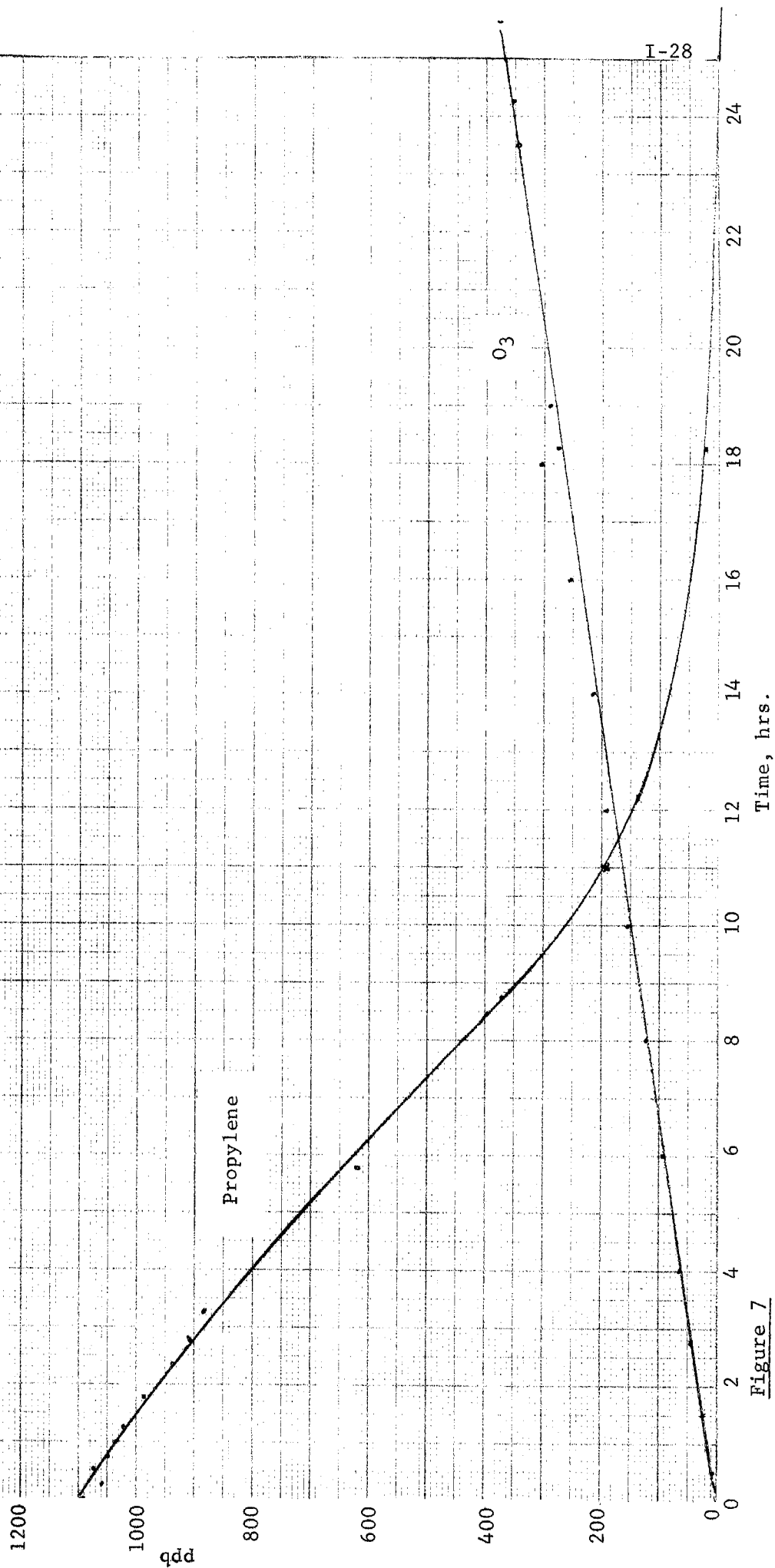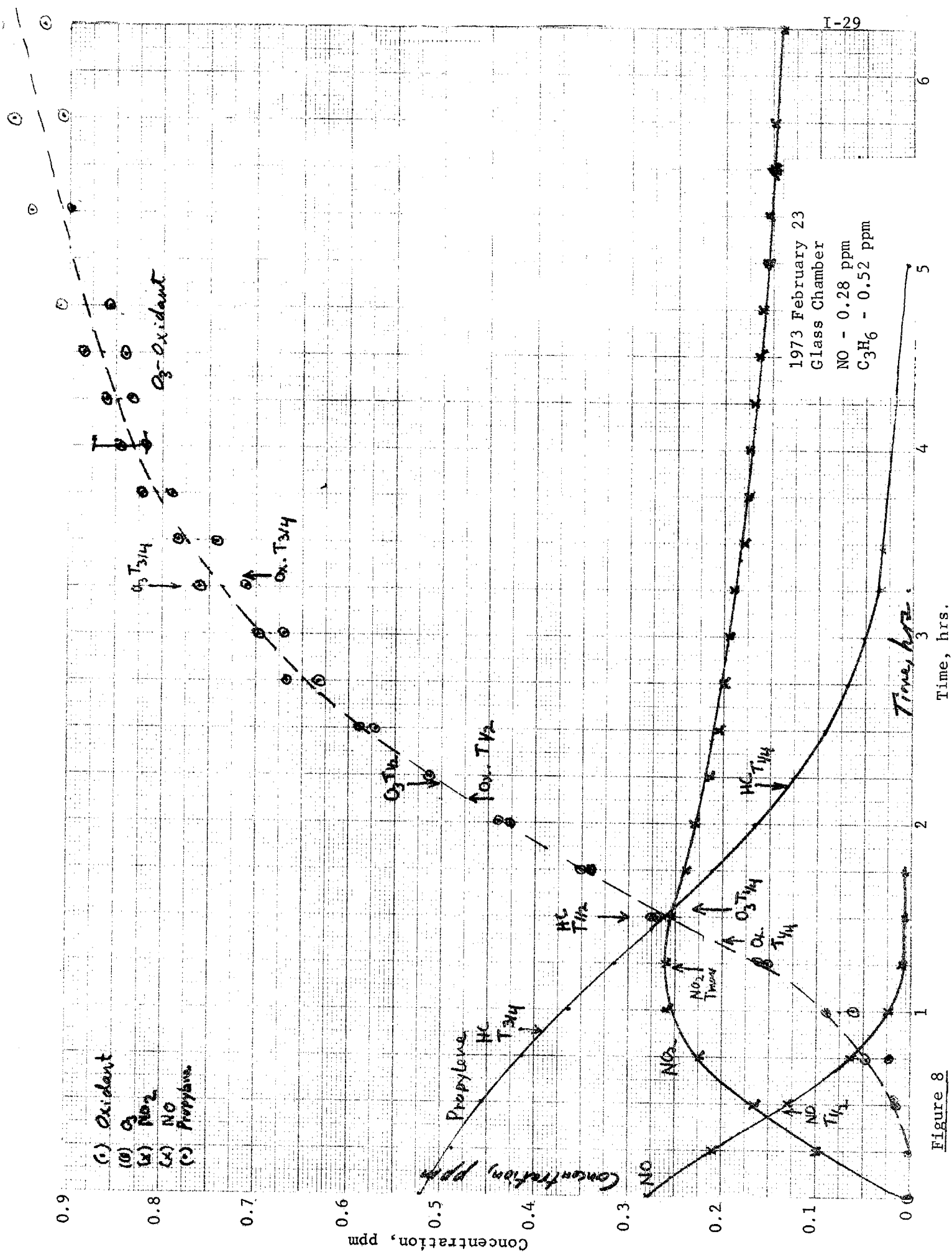
TABLE 8

NO-Propylene Parameters

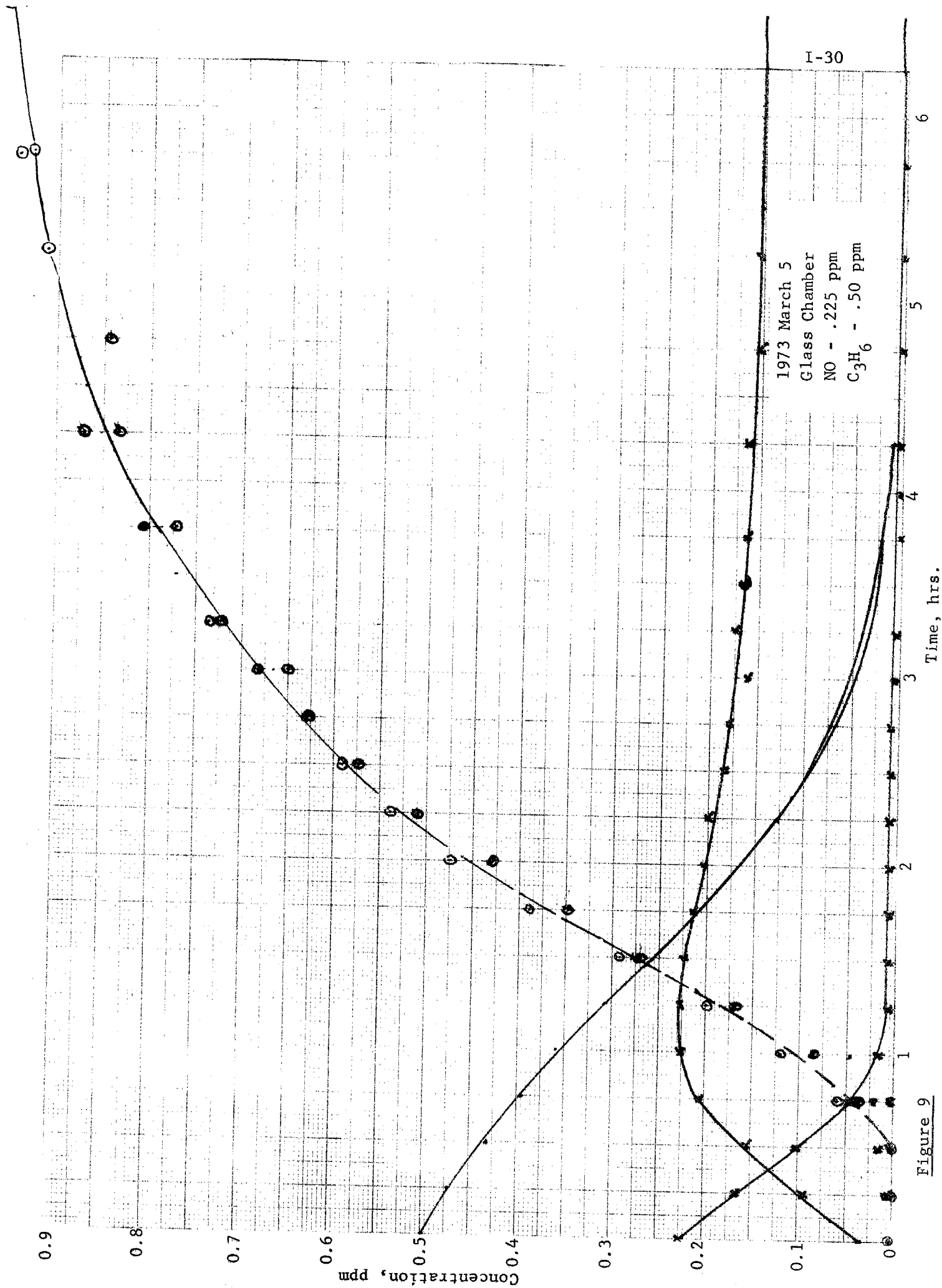|	Date	NO	NO_2	Oxidant
Initial Values (ppm)	2/23	0.29	0.00	0.00
	3/5	0.225	0.035	0.00
Minimum NO (ppm)	2/23	0.005		
	3/5	0.000		
Maximum NO_2 (ppm)	2/23		0.26	
	3/5		0.229	
Maximum Oxidant (ppm)	2/23			0.97
	3/5			1.005

NO_2 and Oxidant Formation Rates

	NO_2		Oxidant	
Date	2/23	3/5	2/23	3/5
$T_{1/4}$ (min)	--	--	$85\frac{1}{2}$	$85\frac{1}{2}$
$T_{1/2}$ (min)	25	23	$127\frac{1}{2}$	129
$T_{3/4}$ (min)	--	--	198	207
T_{max} (min)	70	75	555	525
Av rate (ppm/min)	5.6	4.89	3.8	3.900
Max rate (ppm/min)	--	--	4.3	4.14

Propylene Disappearance Rates

	2/23	3/5
Initial HC, ppm	.520 ppm	.500 ppm
Final HC, ppm	<.0036 ppm	<.005 ppm
$T_{1/4}$ (min)	52.5	52.5
$T_{1/2}$ (min)	91	91
$T_{3/4}$ (min)	133	136
Av rate (ppm/min)	2.83	2.75
Max rate (ppm/min)	3.20	2.99

1973 January 17

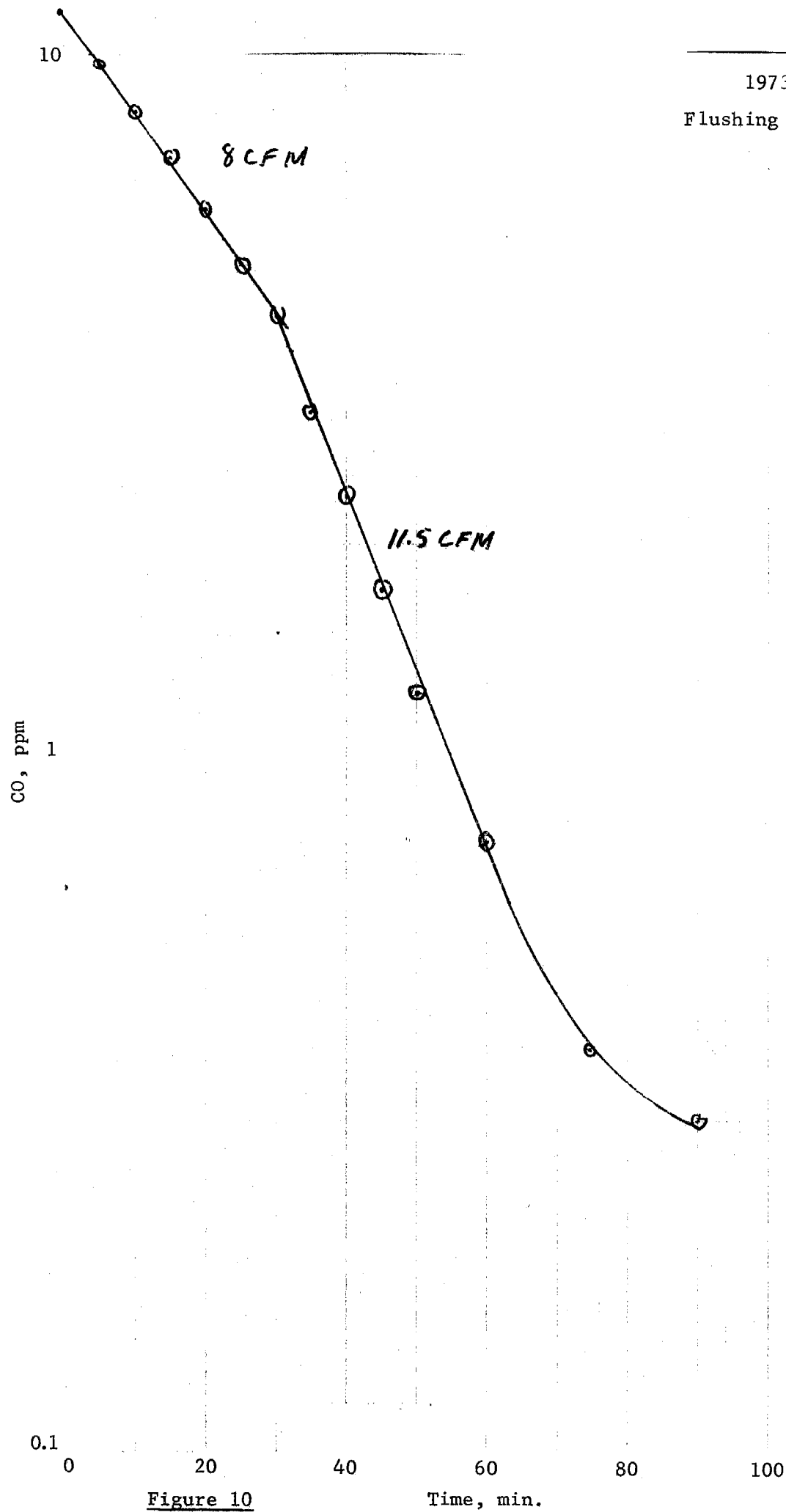Flushing of Glass Chamber

Figure 10   Time, min.

CO, ppm

8 CFM

11.5 CFM

1973 January 16-17
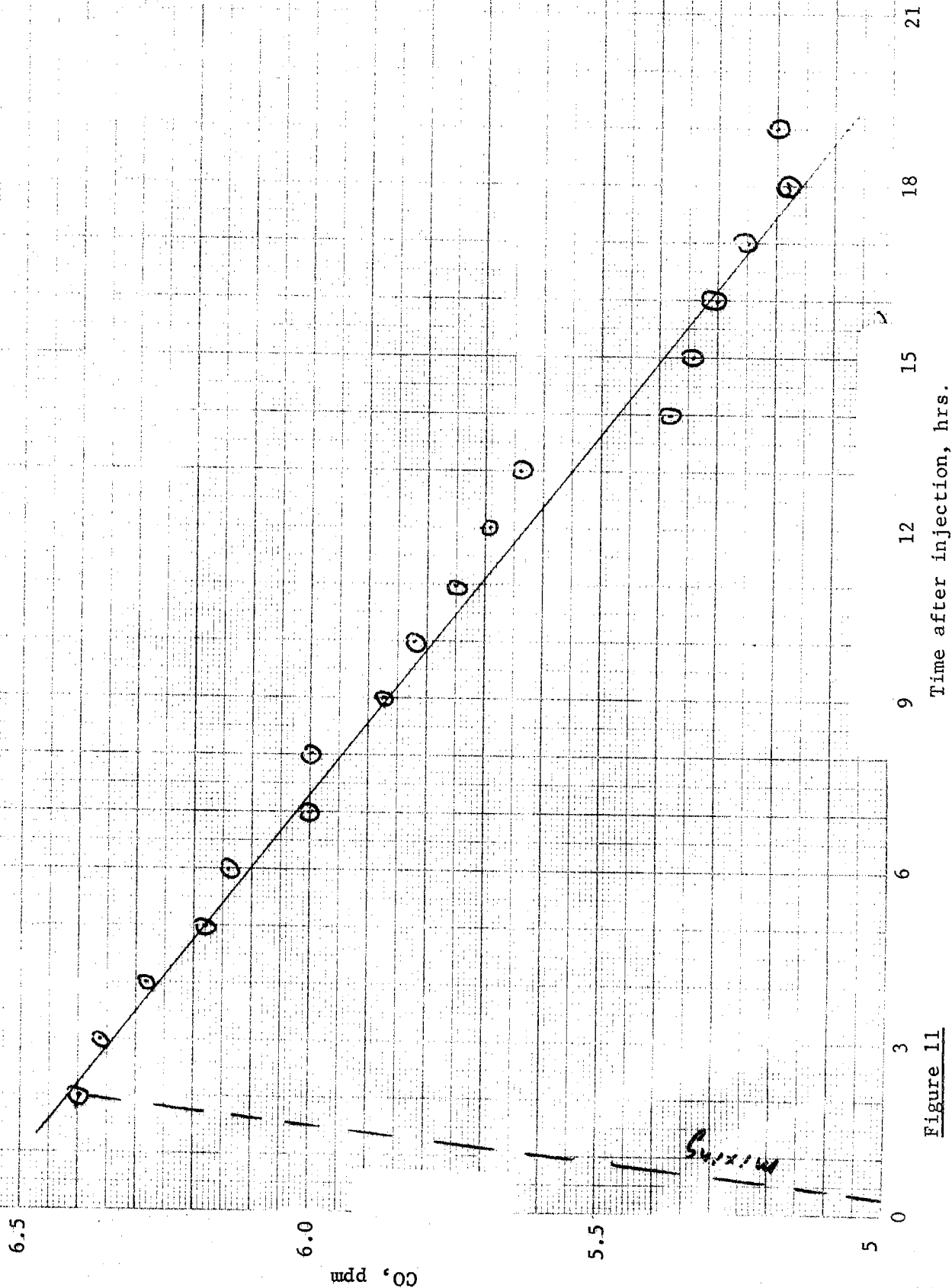
CO decay in All-glass chamber

Sonic Pumps on

Figure 11

I-33

conditions the leak rate cannot be greater than one-half this amount (see Figure 12).

f. Ozone decay in the glass chamber

Figure 12 shows the decay of approximately 1 ppm of initial O_3 in the unirradiated glass chamber. The 0.6% per hour decay rate observed with the lights and sonic pumps off corresponds to a calculated half-life of at least 99 hours, this number being a lower limit owing to neglect of exchange with ambient air due to chamber leakage. With the sonic pumps on the leak rate is approximately 4.3% per hour, with a measured half-life of 8.8 hours. These figures were obtained immediately after the chamber had been conditioned overnight with an initial 10 ppm of ozone (Figure 13). The measured half-life for sonic pumps on in that instance was 10.0 hours. Preliminary data from more recent decay experiments performed without prior conditioning indicate that the very long decay times observed with the sonic pumps off are still obtained, (e.g., a calculated $T_{\frac{1}{2}}$ of 84-hours was obtained in a recent measurement) thus the value presented here is not merely a consequence of the conditioning process, although conditioning will be used periodically as a cleaning method in this chamber.

As expected, the decay times observed when the chamber lights were turned on were substantially shorter (13.3 and 13.4-hour half-lives measured on two separate occasions). At present it has not been determined how much of this acceleration is due to the warmer temperature of the chamber and how much to the presence of ultraviolet radiation. These effects will be quantified at a later date. It should be noted that the decay times for ozone in the dark reported above are larger than those reported for any chamber of which we are aware.

3. Preliminary measurements in the evacuable chamber

Work in the evacuable chamber has been directed towards characterizing the chamber with respect to oxidant formation and solar simulator intensity measurements. These measurements have for the most part not yet been carried out to the same degree of thoroughness as those in the glass chamber, in part, because the unique characteristics of the evacuable vessel have necessitated our taking time to develop ways of compensating for relative pressure fluctuations between the outside atmosphere and the vessel interior. However, we now have enough reliable data to make certain judgements regarding chamber characteristics as follows:

a. Solar simulator

Table 9 summarizes the results of intensity measurements on the 10-KW solar simulator beam in the evacuable chamber:

(~0.6 %/hr decay).

0 ← 1517 hrs.

Sonic pumps off 1500 hrs.

1973 February 14-16

Ozone Decay in Glass Chamber

Just after O₃ Conditioning

~4.3 %/hr (1st 10 hrs)

$t_{\frac{1}{2}}$ = 8.8 hrs.

Data Uncorrected for Dilution.

Sonic Pumps on

Ozone, ppm
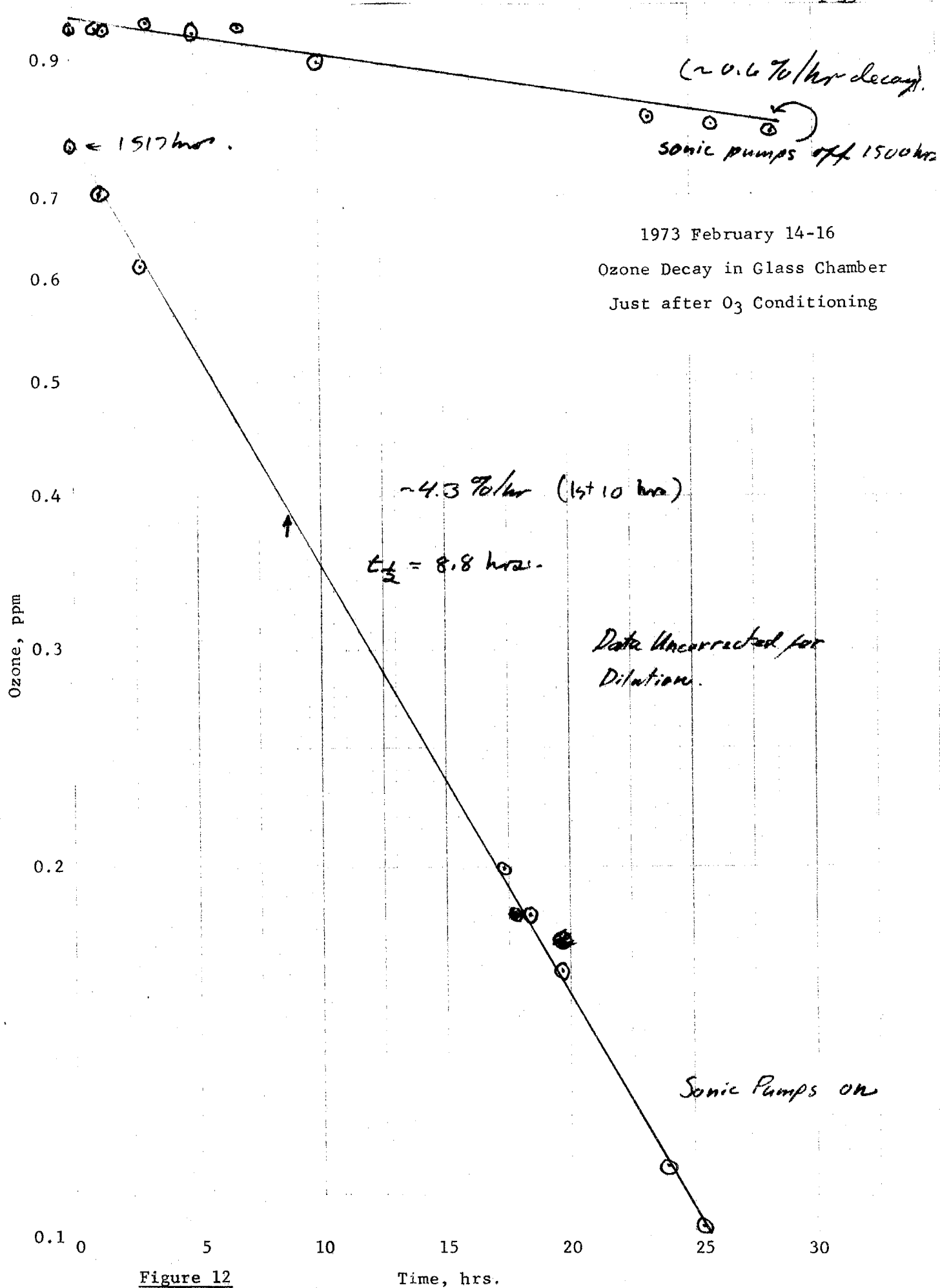
Figure 12

Time, hrs.

1973 February 13-14
Decay of 10 ppm O_3
In Glass Chamber
Sonic Pumps <u>on</u>

$t_{\frac{1}{2}}$ = 10.0 hours

5.0%/hr (1st 10 hrs)

O_3 Concentration, ppm

0   2   4   6   8   10   12

<u>Figure 13</u>   Time, hrs.

Table 9. K_d Measurements in Evacuable Chamber – 10 KW Solar Simulator

No. of Passes of Simulator Beam thru Evacuable Chamber	Filtration	K_d,Min^{-1}
2	Pyrex	0.34
1	none	0.22
2	none	0.40
1	none	0.20
1	none	0.25

Thus, for a single pass of unfiltered radiation the K_d is 0.22 ± 0.03. The highest value, 0.40, is obtained when the beam is returned through the chamber by a retroreflector located outside the far end of the chamber. The most realistic value is obtained with a Pyrex filter in place over the chamber entrance window. By "realistic" it is meant that the spectral distribution of the incoming radiation is altered to more nearly match that of the sun at sea level rather than at high altitude. The 0.34 min^{-1} value obtained for good spectral match compares very favorably with 0.37 min^{-1}, the value representative of Los Angeles noon-day sun.

b. Oxidant formation during photolysis of pure air

Photolysis of pure air resulted in the formation of 0.53 ppm O_3 when the air was let into the chamber after evacuation without an accompanying bakeout. The simulator beam was used without a Pyrex filter pane. When the experiment was repeated after several "cleaning" cycles, i.e. evacuation of chamber accompanied by baking at 100°C, only 0.006 ppm ozone was formed. No ozone could be formed at all when a Pyrex filter was used under these latter conditions. It is on this basis that we attribute some of the formation of oxidant to radiation at wavelengths shorter than 3000Å, and conclude that a Pyrex filter should be used in experiments intended to simulate sea-level phenomena. Two significant implications may be inferred from the dependence on stringent bakeout conditions:

1) The presence of water vapor may well be necessary in trace amounts in order for oxidant formation to occur. In typical clean high vacuum systems water is the major contaminant, but repeated baking can effectively remove water to well below the ppm range if the chamber is not exposed to room air between runs. In this experiment the chamber had been backfilled only with dry nitrogen for several previous runs. With each succeeding pumpdown the vacuum performance improved dramatically until, with the pumpdown just before this run the pressure rose only to 1.2 microns even while baking (compared to 200 microns for first pumpdown and bakeout for a "dirty" chamber). Thus, water may well have been reduced to a level where oxidant formation could not occur.

We note also that difficulty in rigorously preventing the occlusion of water in other chambers may partly account for the disparity reported between different workers examining humidity effects.

       2) Another likely explanation lies in the possible extremely effective removal of reactive contaminants from the chamber walls during the cleaning process. This explanation, too, would be consistent with the impressive pumpdown performance of the chamber. The large amounts of oxidant formed when bakeout was omitted would tend to favor this alternative. Further runs are planned to differentiate between the two possible processes.

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II. FACILITIES

A. Equipment to be Purchased

1. Beckman Model 6800 Air Quality Chromatograph.

For the last seven months a Beckman 6800 air quality chromatograph has been on loan to the SAPRC for the measurement of total hydrocarbons, methane, and CO in the SAPRC chamber facility. We have now acquired sufficient experience with that instrument to be convinced of its reliability and usefulness as an automated instrument for use with the SAPRC chambers, and desire to purchase this chromatograph as a permanent, on-line addition to the facility.

Having a reliable measure of methane, total hydrocarbons and CO makes possible the gathering of information concerning a) the performance of the pure air system; b) the leak rate of the chambers; c) the kinetics of formation of methane and CO in smog-forming reactions; d) the offgassing characteristics of the chamber walls; and e) a check against the accidental introduction of unwanted hydrocarbon contaminants not otherwise detectable in our analysis procedure for individual hydrocarbons.

Several factors dictate the choice of the Beckman 6800 as the appropriate instrument for the above measurements.

a. No additional start-up time is required, since the instrument is already in place and sampling from the chambers.

b. This particular instrument has been modified by Beckman personnel at no cost to SAPRC in order to increase its maximum sensitivity to better than 1 ppm full scale on all components.

c. The sensitivity to CO inherent in this automated instrument makes it the logical choice for our routine analysis of this compound, rather than non-dispersive infrared techniques.

d. One of our staff (Dr. Wendschuh) has trained with the Beckman personnel at their factory for a week on the 6800. He is thus very capable of maintaining this instrument as part of his duties in the chamber analytical section.

e. We have had continuing cooperation with Beckman personnel in incorporating the latest changes in design as they are developed, in order to ensure maximum sensitivity and reliability over the longer term. We can state from our experience to date that after its initial shakedown, this particular instrument has been virtually maintenance-free. We consider it a worthy addition to the SAPRC chamber instrumentation.

2. Tetrahedron Associates Data Manager: Data Logger.

Handling of the data output during the course of the chamber project is determined in accordance with the following objectives:

a. Documentation and retention of data with respect to all parameters measured during the course of the chamber runs (i.e., temperature, oxidant, ozone, etc.)

b. Reduction of data to a form suitable for rapid evaluation and clear presentation.

c. Conversion of data to a form compatible with the computing equipment used at SAPRC and, ultimately, in other laboratories as well.

Currently, raw data is gathered by direct recording on strip charts or by manual reading of instrument dials. Numbers are abstracted by hand from the charts, corrected for scale expansion, zero drift, calibration factors, etc. and replotted by hand as a function of time. Time generally does not permit the direct examination of the interrelationship of different variables with each other as well as with time. Thus, for example, it might be useful to plot CO vs. NO_x or oxidant or total hydrocarbons during the course of an experiment, yet point-by-point graphs are prepared manually only at great expanse in time and at some risk of error owing to the manual transposition of data into the requisite forms.

We propose, therefore, to take the first steps towards gathering all of our chamber data in a form permitting the rapid, reliable attainment of all three of the objectives outlined above. Data will be read directly into a device which rapidly and periodically samples all of the chamber instrumentation; the data are stored in a form which will permit the non-destructive readout of any variable versus any other or versus time. In addition, storage of the data on magnetic tape cassettes will make possible the accurate transcription of chamber results into forms which can be digested by computers for inclusion in atmospheric models and kinetic mechanism studies.

A compact device which will permit the data processing described above is the Data Manager II, manufactured by Tetrahedron Associates. This instrument accomplishes these objectives in the following manner:

a. Incoming data (up to 14 channels plus time) are digitized and stored on a magnetic tape cassette, with signals automatically ranged and stored for readout at any desired scale expansion. Data from any point during a run can be accessed quickly using a "time search" feature.

b. Data output from any channel can be plotted against any other channel by a straightforward readout into an x-y recorder. Thus, the data are easily evaluated in analog form and in many cases can be presented without further manual replotting.

c. The stored digital information can be made computer-compatible by a proper choice of interfacing. This will eventually permit direct access to the data for modeling purposes.

The initial cost of the system is moderate at $10,000 (cost breakdown given below), and operating costs are expected to be negligible, since no computing personnel are required in the day-to-day chamber operations. The cost breakdown is as follows:

Data Manger	$7,800.00
Teletype interface	1,000.00
x-y plotter	1,050.00
	9,850.00
California tax	492.50
	$10,342.50

Finally, it should be pointed out that the technology data processing equipment is expanding at a rapid rate. Therefore, we propose to continue an exhaustive search of available instrumentation in order to ensure that the equipment purchased at the time funds are released is indeed the best available.

B. Existing Facilities

Specific equipment presently available is broken down into five categories and listed below:

The SAPRC Smog Chamber Facility.
Equipment Belonging to Our Research Groups.
Major Departmental Instruments and Facilities.
Equipment Available at the University of California, Statewide
  Air Pollution Research Center.
Computing Facilities.

The SAPRC Smog Chamber Facility

The new ARB-funded smog chamber research facility at SAPRC consists principally of two smog chambers (each of approximately 200 cu. ft. volume) and a 10-KW solar simulator (conversion to a 20-KW system in pending). One chamber is of "conventional" design, with all-glass walls and fluorescent lighting similar to that used in previous studies (see Figure II-1). The second is an evacuable chamber with teflon-lined walls and quartz-end windows which transmit 90% of the UV radiation produced by the solar simulator down to 2400 $\overset{o}{A}$ (see Figure II-2).

A. The two chambers are paired in a single facility, incorporating the following subsystems in common:

1) Air purification system
2) Dedicated analytical instruments
3) Solar simulator

B. The evacuable chamber:

1) Is a state-of-the-art facility which can be cleaned by evacuation and heating.

2) Contains an integral optical system for long-path IR (200-meter) and UV (15-meter) spectrophotometry for non-destructive in-situ analysis of trace quantities of air pollutants.

3) Can be routinely heated under vacuum to 100° C between runs in order to remove occluded contaminants from the walls. It is free from hydrocarbon contamination because a four stage totally hydrocarbon-free pumping system is used. (This feature exists on no other smog chambers currently in operation.) The four stages consist of:
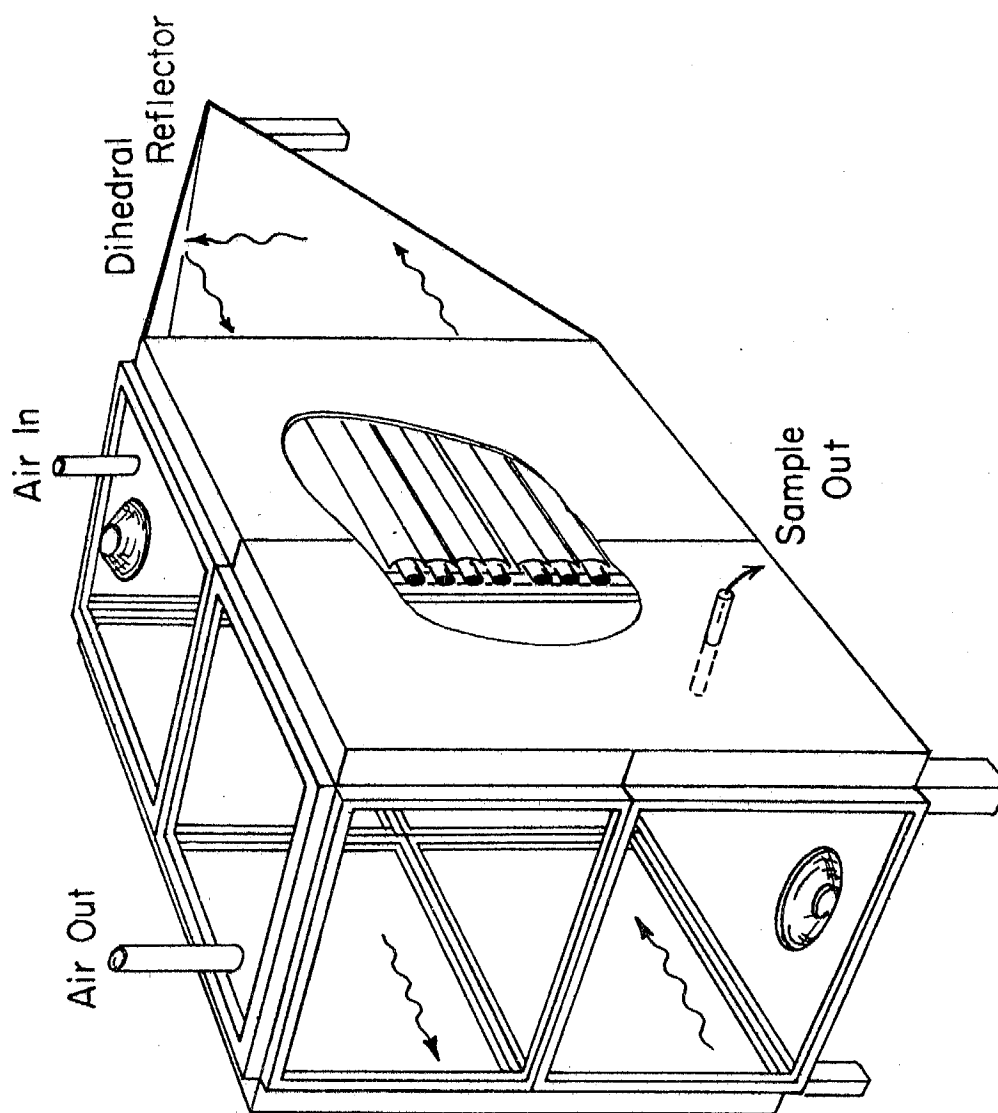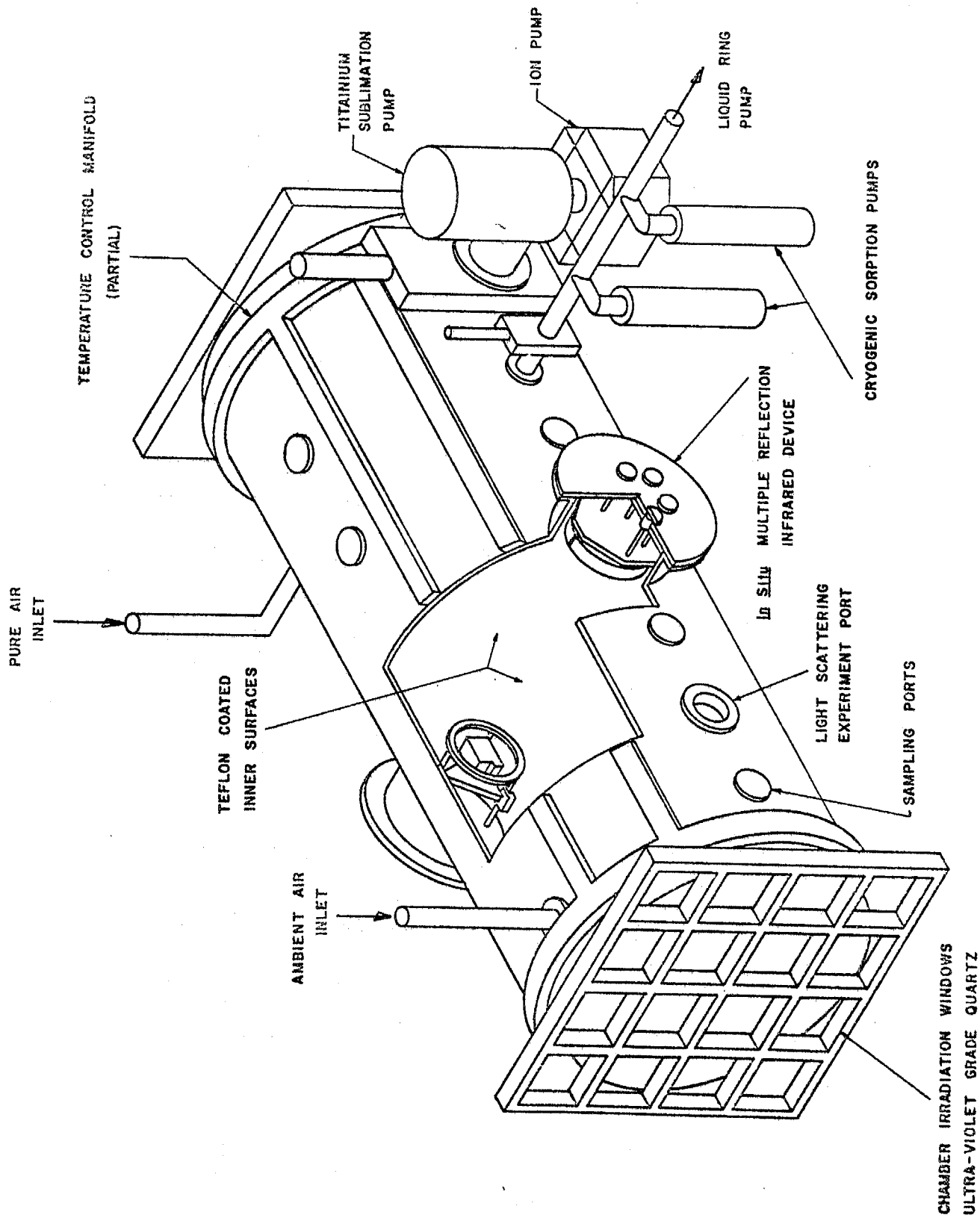
Figure II-1. SAPRC All-Glass Smog Chamber

Figure II-2, SAPRC Evacuable Smog Chamber

a) A SIHI liquid ring pump which uses water, not oil, as its working fluid and which roughs the chamber to approximately 10 torr.

b) A manifold of three triple-vac sorption pumps which further rough the chamber to a pressure of 1 μ.

c) The first high-vacuum stage is a titanium sublimator which is primarily responsible for reduction in pressure through the 10^{-4} and 10^{-5} torr ranges.

d) The final high-vacuum stage is an ion pump which begins to operate efficiently at pressures of 10^{-6} torr and below. With the system described the evacuable chamber has reached a base pressure of 1×10^{-7} torr.

4) Achieves inertness to atmospheric reactants by having only FEP teflon and quartz exposed to the chamber atmosphere.

5) Has temperature variation capabilities from -40° C to $+100^\circ$ C, with temperature control to $\pm 1^\circ$ C throughout the chamber shell in order to minimize convective transport of reactants to chamber walls, helping to assure close simulation of ambient atmospheric conditions at any altitude between ground level and 25 km.

6) Has windows of high-quality quartz to admit a collimated beam of simulated solar radiation. These windows have very high transmission efficiencies (>90%) throughout the visible and UV regions (down to at least 2400 Å). Exit windows help temperature control by allowing heat dissipation outside the chamber.

7) Minimizes photochemistry occurring at the walls because the simulator beam does not directly contact the chamber sidewalls.

8) Can be evacuated to a nominal base pressure of at least 10^{-6} torr permitting simulation of pressure to very high altitudes.

C. The solar simulator (shown in its present configuration in Figure II-3):

1) Provides one solar constant in the UV and visible region.

2) Will have beam collimation to 1°, providing exceptional beam uniformity.

3) Can provide some control of spectral and intensity distributions during a run, including programming of sunrise to sunset cycles. This is a unique feature permitting closer simulation of diurnal behavior than has previously been possible.

4) Is the only solar simulator designed especially for use in air pollution applications, resulting in a uniquely suited facility at a fraction of the cost of most solar simulator systems.

5) Will be upgraded to the 20-KW, sector equipped system shown Figure II-4.

LIQUID SPECTRAL FILTER

TRI-CHROIC SPECTRAL FILTER

QUARTZ FOCUSING LENS

FOLDING MIRROR (FLAT)

XENON ARC LAMP AND COLLECTOR

SECONDARY MIRROR

OPTICAL AXIS
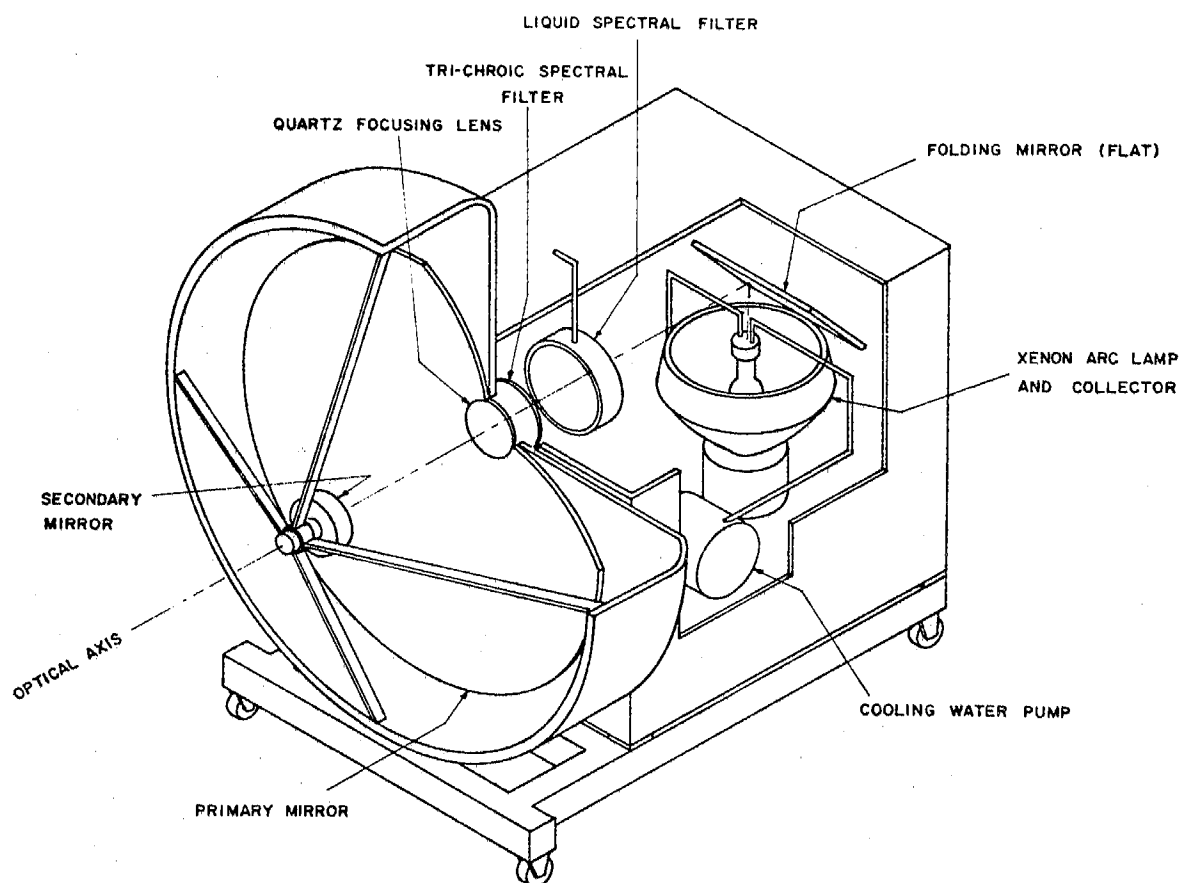
COOLING WATER PUMP

PRIMARY MIRROR
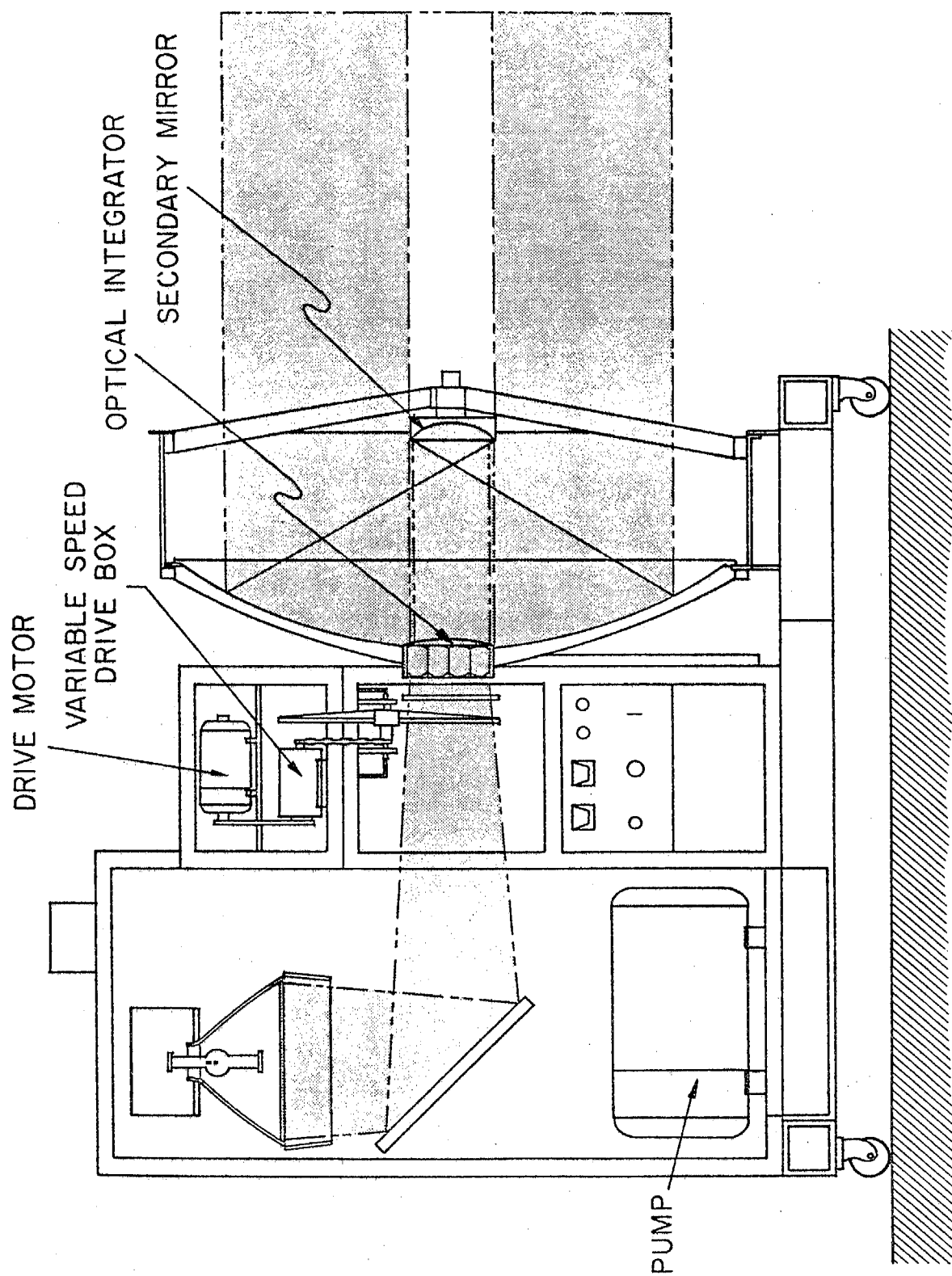
Figure II-3. SAPRC Solar Simulator

Figure II-4. Proposed configuration of SAPRC solar simulator modified to 20 KW system and equipped with optical integrator and rotating sector.

D. The all-glass chamber:

    1) Has a novel irradiation system consisting of banks of fluorescent "black lights" fitted with a reflector and temperature control feature permitting greater spatial uniformity and intensity control than has existed in previous systems.

    2) Is stirred by means of Teflon-coated sonic pumps.

E. The air purification system:

    1) Has been tested and shown to provide background air which is pure enough to permit studies at pollutant concentrations as low as those specified by the Federal air quality standards (i.e., background levels <1 ppb for most pollutants).

    2) Provides dynamic mixing of all pollutants to be studied.

    3) Provides control of residence-time over the range of 20 minutes to infinity.

    4) Provides control of air temperature over the range 15° to 45° C and humidity control between zero and 100%

F. Capabilities of the SAPRC in-situ LPIR-UV spectrometer system are as follows:

    1) Sensitivity limits in the IR are up to 100 times better than conventional 40-meter LPIR instruments. This results from:

        a) Higher reflectance mirrors (R = 0.993).
        b) Greater detectivity (cooled detectors).
        c) Greater attainable resolution.
        d) More light through-put due to advanced monochromator design.

    2) Such sensitivity will permit, for the first time, utilization of the LPIR technique in chamber experiments at the Federal Air Quality Standard concentrations.

    3) Higher resolution and greater sensitivity will aid in the detection and identification of previously unobserved species.

    4) Routine path-length selection during experiments to permit simultaneous monitoring of strong and weak absorptions.

    5) Both LPIR and LPUV capabilities are provided at a cost comparable to that of either a commercial IR or UV spectrometer.

G. Analytical instrumentation for the chamber facility are:

1) Three gas chromatographs for analysis of individual hydrocarbons, duplicating the highly successful techniques developed by Stephens and Burleson

2) One Mast oxidant meter

3) Two Dasibi ozone analyzers

4) One Bendix chemiluminescent $NO-NO_2-NO_x$ monitor

5) One Aerochem $NO-NO_2-NO_x-O_3$ chemiluminescent instrument

6) One 200-meter LPIR spectrophotometer

7) One Beckman model 6800 chromatograph for automated methane, CO, and total hydrocarbon analysis (on load)

Equipment Belonging to Our Research Groups

Specialized and conventional research equipment on hand in the Principal Investigator's basic research laboratories in the Department of Chemistry and at SAPRC, includes:

Germanium photodiode
Monochromators
Photomultipliers
Lock-in amplifiers
DC amplifiers
Logarithmic recorder
Perkin-Elmer long-path infrared spectrophotometers
Cary 15 UV-visible spectrophotometer
CEC model 21-620 mass spectrometer
Phosphorimeter
Vacuum systems for both flow and static gas-phase studies
Gas chromatographs
Annular spinning-band distillation columns
Mast ozone meter with recorder

Major Departmental Instruments and Facilities

Specific major instruments on hand in the Chemistry Department and available for use in this NSF-RANN program include:

Varian A-60, A-60D, HR-60, HA-100 nuclear magnetic resonance
    spectrometers with a Computer of Average Transients
Perkin-Elmer Hitachi RMU-6D double focusing mass spectrometer
Perkin-Elmer Differential Scanning Calorimeter
Perkin-Elmer LR-1 laser Raman spectrometer
Beckman scintillation counter
Beckman low beta counter
Beckman amino acid analyzer

Beckman ultra-centrifuge
Durrum-Jasco optical rotatory dispersion and circular dichroism
  spectrometer
General Electric XRD-511 X-ray diffraction apparatus
Automated Picker X-ray diffractomer
McPherson vacuum ultraviolet monochromator ultraviolet and
  infrared spectrophotometers
Automated high-pressure reaction facility

Equipment available in other departments on the campus includes an RCA electron microscope, a Collins Liquid Helium Cryostat, and a millicurie laboratory.

Equipment Available at the Statewide Air Pollution Research Center

The Center's equipment available for use in this NSF-RANN project includes:

Spinning-disc aerosol generator
Beckman GC-5 gas chromatograph with helium ionization detector for
  CO measurements
Perkin-Elmer 137 NaCl infrared spectrophotometer (used to compare
  synthetic aerosols with those found in natural smog)
SO_2 analyzer-recorder
Bausch and Lomb 40-1A dust counter with readout and digital printer
  for aerosol counting and sizing
Sinclair-Phoenix smoke photometer
Mast ozone meter with recorder
Bausch and Lomb SPEC-20 colorimeter
Calibrated gas chromographs for hydrocarbon analysis

The SAPRC facilities also include an electronics shop specifically equipped for maintenance and construction of air pollution related instrumentation. In addition, excellent glass shop, electronics shop, and machine shop facilities are also available in the UCR Departments of Chemistry and Physics.

Computing Facilities

The UCR Computing Center was established in 1963 to aid the education and research programs of all academic departments. Its facilities, open to graduate students, faculty and staff engaged in supported and unsupported University research have been continually upgraded and expanded. The present facilities include an IBM 360 Model 50 OS Release 21 with 384K bytes of fast core storage, six 2311 disk drives with 7.5 million bytes per disk, three tape drives and a large configuration of input/output software including a Calcomp plotter. The Computing Center has received campus approval to extend the core memory to 768K, to obtain eight 2314 disk drives with 29.17 million bytes per disk and a 1000 lines per minute 1403-H1 printer. Pending universitywide approval, this equipment will be installed approximately June, 1973. The computer can also be accessed through medium-speed IBM 2741 Communications Terminals in the Chemistry Department and at the SAPRC. Additional small computers (i.e., PDP-12) and off-line equipment are available. Thus, the UCR computing facilities are entirely adequate to support the proposed research.

III. MANAGEMENT PLAN

A. Organizational Assignments

The overall organizational structure responsible for the conduct and management of the proposed project is depicted in Figures III-1 and III-2.

Responsibility for the planning, supervision, and coordination and execution of this research program resides with the Principal Investigator, Dr. James N. Pitts, Jr. This applies to the technical and scientific aspects of the effort as well as to its overall management. Since the Principal Investigator is also Director of the Statewide Air Pollution Research Center, he is readily able to integrate the efforts and results of all other programs being undertaken at the Center with those of the program being proposed here.

Reporting directly to the Principal Investigator is the Chamber Program Manager, Dr. Arthur M. Winer, who is responsible for supervising all aspects of the daily execution of the research program.

Key functions in the operation of the facility are acquisition and analysis of analytical data, directed by Dr. Paul J. Bekowies and operation and maintenance of the two SAPRC chambers and the solar simulator, carried out by Dr. John McAfee who also has prime responsibility for LPIR and LPUV spectroscopy. Working closely with Dr. McAfee in chamber operations is Dr. Peter Wendschuh who has a unique training, with degrees in both chemical engineering and organic chemistry.

The staff is further augmented by two Research Associates, William Long and Sharron Harris, and by graduate student, Christopher Pate.

Two additional key members of the chamber oganization are Dr. Alan Lloyd and Dr. George Doyle. Dr. Lloyd is Assistant Director of the SAPRC and an authority in the critical evaluation of kinetic data. He will direct the analysis of ambient air data and the computer modeling studies associated with the chamber studies. Dr. Doyle, is the Senior Data Analyst for the chamber research program and has over two decades of experience in air pollution research with a strong background in theoretical aspects of the chemistry and physics of photochemical air pollution.

More complete descriptions of the backgrounds, qualifications, and experience of the chamber staff are furnished in Section VI, Curriculum Vitae.

Augmenting the expertise of the chamber research team are Dr. Edgar Stephens, an internationally recognized authority in air pollution research, and Dr. William Kuby, Associate Dean, College of Engineering, University of California, Santa Barbara, who will be on sabbatical leave from that campus and who will be assisting in the development of the computer modeling program. In addition, we have close liaison with two well-known experts in combustion engineering, Professors Robert Sawyer and Scott Samuelson of the University of California, Berkeley and Irvine campuses, respectively. We have also been in consultation with the Scott Research Laboratories in San Bernardino.
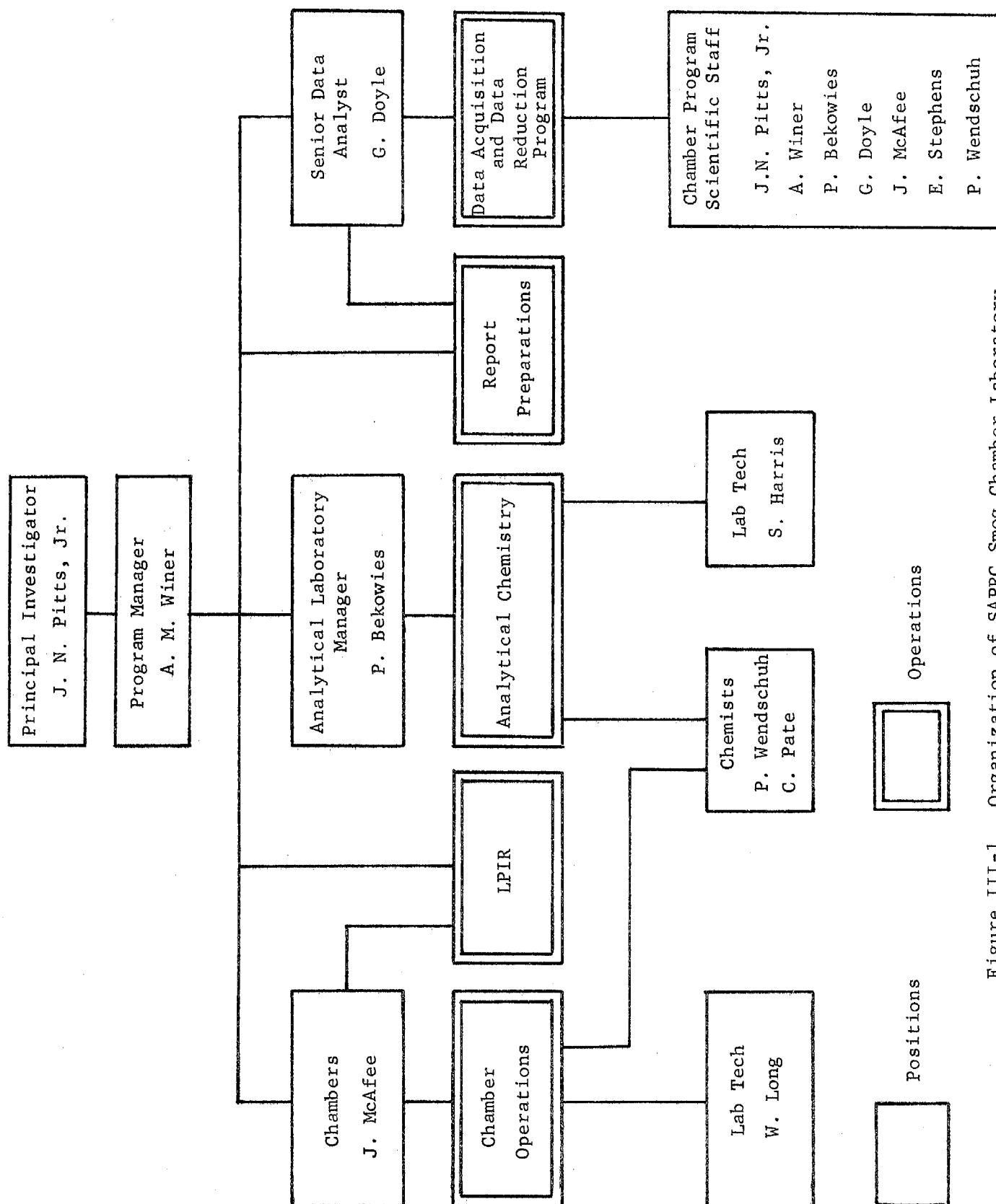
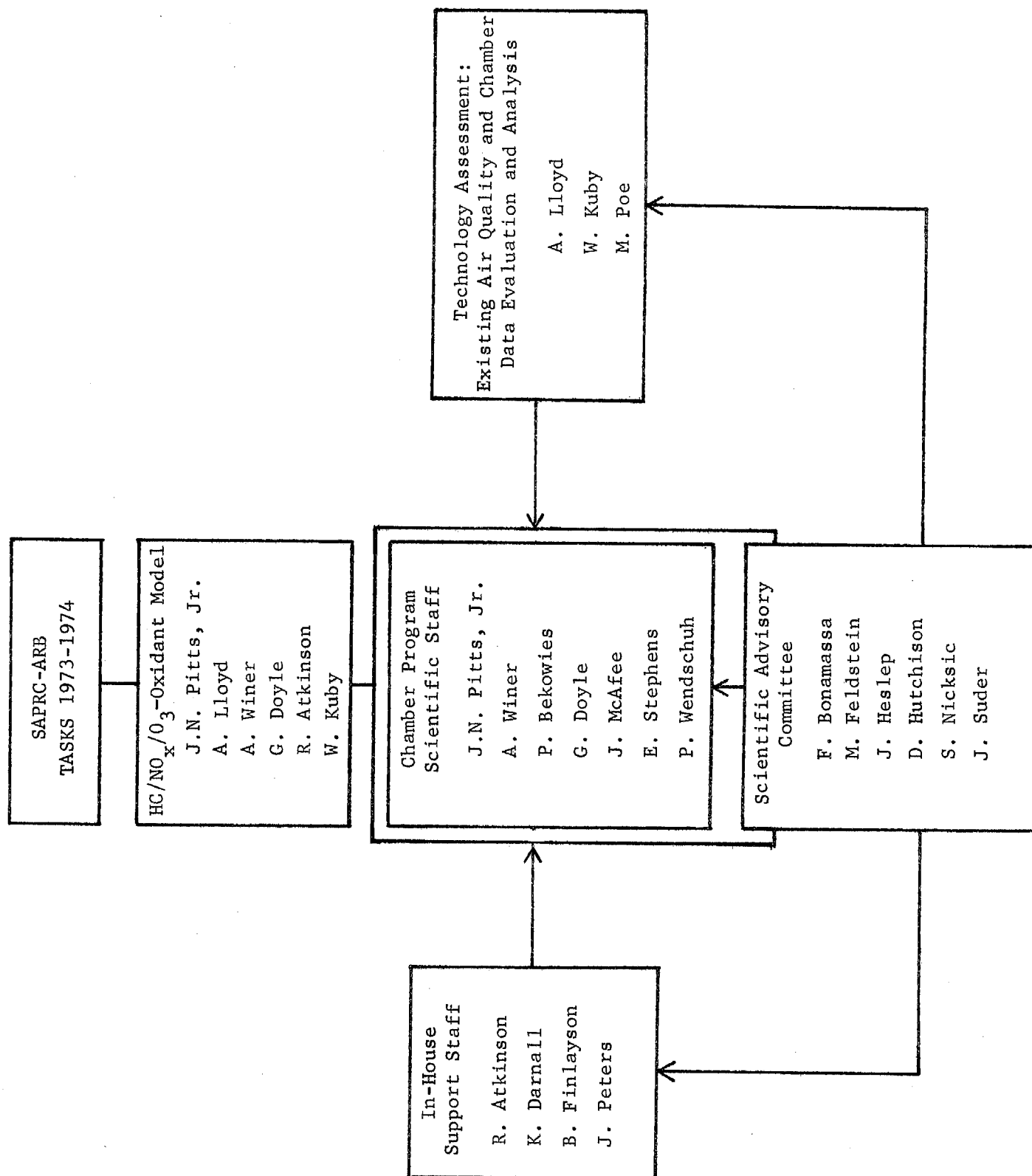Figure III-1. Organization of SAPRC Smog Chamber Laboratory

Figure III-2. Organization for SAPRC-ARB Project

Additional expertise will be furnished to the chamber program at no cost to the ARB from members of the Principal Investigator's fundamental research laboratories in the UCR Department of Chemistry. Dr. Roger Atkinson is an expert in gas-phase reaction kinetics having studied with K. H. Welge, R. J. Cvetanovic, and B. A. Thrush with emphasis on ozone and O-atom reactions with olefins as well as studies of H-atom and OH radical reactions. Dr. Karen Darnall is an authority on the chemical reactions of PAN and PBzN with a strong background in the photochemistry of air pollution. Dr. John Peters has carried out extensive investigations on the chemistry of singlet oxygen and is leading an effort to detect this species in ambient atmospheres. Ms. Barbara Finlayson will shortly be completing her Ph.D. research concerning chemiluminescent ozone olefin reactions and will remain at UCR-SAPRC as Postdoctoral Fellow for an additional year.

Finally, we will continue to look to members of the Air Resources Board such as Mr. Dale Hutchison, Mr. Frank Bonamassa, and Mr. Jack Suder (Technical Monitor for the chamber program) and to the other members of the Chamber Science Advisory Committee, Mr. M. Feldstein, Dr. J. Heslep, and Dr. S. Nicksic for their guidance and technical input concerning present and future chamber programs.

The interrelationship of these various organizational members and units, as well as the interaction between the SAPRC-ARB program and other SAPRC programs, is depicted in Figure III-3.

B. Progress Reviews

Regular monthly progress reviews will be held in which the Principal Investigator, in conjunction with the Program Manager and chamber staff, will assess the status of the research program. These reviews will serve to define progress toward achieving the specific aims of the program, and as opportunities to revise the goals or methods of procedure if necessary.

C. Status Reports

Quarterly progress reports will be submitted to the Air Resources Board in which progress made during the preceding three months will be summarized. Any problems or difficulties encountered will be discussed with proposed solutions and implications for meeting schedule. Anticipated work to be conducted during the following quarter will be noted.

A final report summarizing all work accomplished with conclusions, and recommendations for further work, will be submitted for ARB review at the end of the contract period.
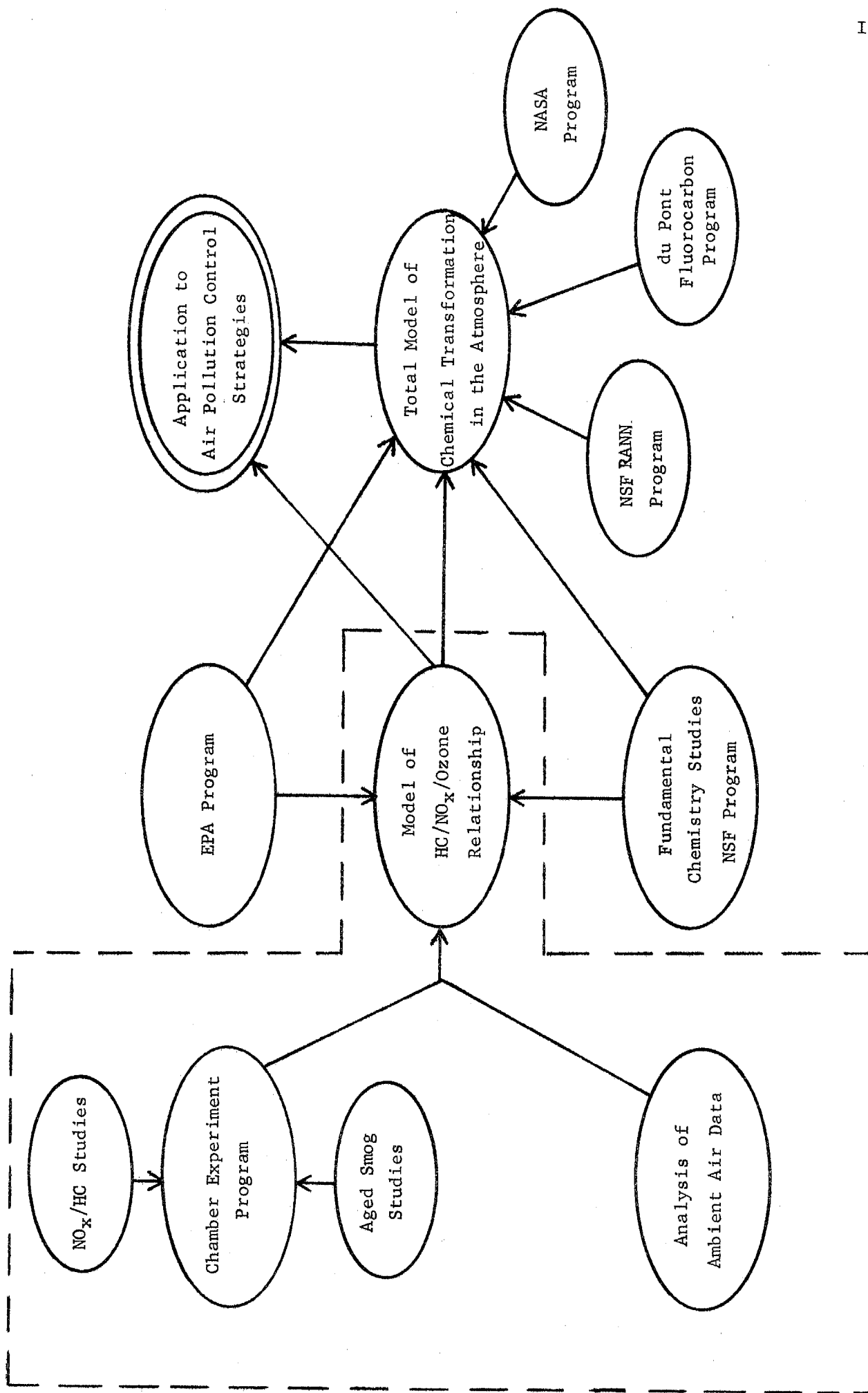
Figure III-3. Relationship between ARB program and other SAPRC programs

IV. RELATED RESEARCH

A. Chamber Studies

Supplement to EPA #800649. A chamber research program has been formulated which will provide direct input to a modeling program being conducted by the Environmental Protection Agency. An initial major effort will be made to quantify the operating characteristics of the SAPRC evacuable chamber and solar simulator. Following this, a systematic investigation of the time- and variable-dependent behavior of simple photochemical systems undergoing simulated solar irradiation will be made. The program will include a study of the effects of aldehydes and, on a factorial design basis, the irradiation of NO_x-hydrocarbon systems, beginning with a single hydrocarbon and building through systems of NO_x plus two- and three-component hydrocarbons. A special effort will be made to control and monitor variables often not well characterized in past chamber studies, such as relative humidity, temperature, purity of matrix air, and spectral distribution of photolyzing radiation.

B. Programs Under the Principal Investigator

1. Current Programs

a. EPA #800649. Reactions of possible importance in photochemical air pollution are being investigated with a variety of techniques over a wide range of pressures and concentrations in homogeneous and heterogeneous vapor, liquid, and solid systems. Research includes selected aspects of the photochemistry, spectroscopy, kinetics, and mechanisms of photooxidation of atmospheric pollutants, including PAN, monocyclic aromatic hydrocarbons, and partially oxygenated hydrocarbons, such as aldehydes and ketones. Investigations of the thermal and photochemical reactions of oxides of nitrogen, particularly the NO_2-catalyzed isomerization of olefins, are continuing. Long-path (10-200 m) IR and UV techniques are being used to identify unstable intermediates and products in the ppm range. Applications of our research to improved air pollution monitoring instrumentation are being studied.

b. NSF Grant GP 34524. The gas-phase room temperature reactions of ozone with simple olefins are being investigated in order to:

1) Elucidate the mechanism of production of the observed chemiluminescence.

2) Determine the general mechanism of reaction of gas-phase, ozone-olefin reactions.

3) Extend the chemiluminescent and mechanistic studies of ozone-olefin reactions to the reactions of ozone with other simple organic compounds, such as sulfides, aldehydes, etc.

Research is continuing to further elucidate the role of singlet molecular oxygen as an environmental oxidant. Specifically, the importance in photochemical smog of reactions which produce and consume $O_2(^1\Delta_g)$ are being evaluated.

Spectroscopic techniques using a germanium photodiode detector sensitive at 1.27μ are being used to determine the production of $O_2(^1\Delta_g)$ by four paths now confirmed as being possible in real atmospheres: 1) gas-phase photosensitized reactions; 2) gas-phase reactions of organic compounds with ozone; 3) photolysis of ozone at 3130 Å, and; 4) oxygen-enhanced absorption of organic pollutants. Studies on the effects of externally generated $O_2(^1\Delta_g)$ on biologically significant molecules continue to be carried out. A new, "clean" source of $O_2(^1\Delta_g)$ in aqueous solutions--a peroxy chromate, K_3CrO_8-free of complications from oxygen atoms and H_2O_2 present in other systems, has been discovered. A preliminary investigation of the chemical and biological utility of the peroxy chromate as a singlet oxygen source is under way.

Concurrent with the laboratory studies, the relative importance of singlet oxygen, ozone, and oxygen atoms as environmental oxidants are being evaluated.

    c. __NASA.__ In cooperation with the NASA-Ames Research Center at Moffett Field, the SAPRC is currently carrying out airborne monitoring studies of pollutants, using an instrumented Cessna aircraft.

The primary objective of this study is to obtain detailed three-dimensional measurements of an urban atmosphere, using airborne instrumentation to validate specific aspects of an air pollution photochemical model. In particular, the relationship between atmospheric ozone, nitric oxide, nitrogen dioxide and incident solar ultraviolet radiation from ground level up to approximately 20,000 ft. is being determined. Particular emphasis will be given to the effects of other atmospheric phenomena; i.e., PAN, water, and carbon monoxide levels, as well as wind vectors on these relationships. This study has already provided some of the first information on "3-D" mapping of pollutants in the atmosphere. The results will be utilized in conjunction with ground-based data to validate models of photochemical air pollution in real atmospheres.

    d. __NSF Basic Chemistry.__ A coordinated, basic research program is proposed that involves studies of the rates, mechanisms, products, and intermediates for gas-phase oxidations of selected organic molecules by ozone, hydroxyl radicals, oxygen atoms, and singlet molecular oxygen, $O_2(^1\Delta_g)$.

This proposal includes continuing our present ozone-olefin studies and extending initial studies of the chemiluminescent reactions of ozone with selected organic compounds; an in-depth evaluation of K_3CrO_8, a new source of singlet oxygen in aqueous solutions recently discovered in our laboratory; $O_2(^1\Delta_g)$ production from gas-phase reactions of ozone with alkyl ethers and other organic molecules; and the reactions of $O_2(^1\Delta_g)$ with electron-rich molecules, such as tetramethoxyethylene.

A major new effort will be the determination of rate constants for the gas-phase elementary reactions of ground state oxygen atoms and OH radicals with selected olefins and simple monocyclic aromatic hydrocarbons by both vacuum UV flash photolysis and modulation and phase-shift techniques.

2. Proposed Program

a. <u>Chemical Transformations in Photochemical Smog and Their Applications to Air Pollution Control Strategies</u>. Funding sought from NSF-RANN.

A two-year, mission-oriented, applied research program is proposed to investigate key reactions of chemical and biological significance in photochemical smog. Its overall goal is the generation of an experimentally validated computer model for chemical transformations in simulated smoggy atmospheres which is directly applicable to the real atmosphere. The model will provide a substantially more accurate, comprehensive and usable scientific base than presently exists for current and proposed air pollution control strategies developed as a consequence of the national Clean Air Act and its amendments. The SAPRC model will be based on (1) a comprehensive evaluation of <u>existing</u> kinetic, mechanistic, and product information, (including computer models) from the EPA, industrial and other laboratories, and (2) a carefully selected series of detailed and exploratory experiments coordinated into one research effort in our laboratories.

Specific objectives include detailed smog chamber studies to assess (1) the reactivities of the exhaust gas from a test I.C. engine run on the gaseous fuels LPG and CNG (vs. gasoline), and (2) the atmospheric impact not only of the major primary pollutants--hydrocarbons, NO_x, and CO--but also of certain often ignored, but <u>potentially important</u> primary and secondary contaminants such as (a) halogens, (b) ammonia and nitrous oxide, products from certain test catalytic emission control devices, and (c) highly toxic unsaturated carbonyl compounds such as acrolein and ketene. Studies will be conducted in the recently completed SAPRC smog chamber facilities funded by the California Air Resources Board including a unique, 5300-liter evacuable chamber, illuminated by a 20 KW solar simulator and incorporating state-of-the-art 200-meter LPIR and 15-meter LPUV spectrophotometers.

Exploratory studies also include use of rotating sector and molecular modulation techniques for chamber studies of free radical chain carriers in photochemical smog and an investigation of the effect on photochemical smog production from an increase in solar UV radiation that <u>might</u> result <u>if</u> there were a destruction of part of the ozonosphere from extensive SST flights. These are coordinated with detailed studies of the chemistry of secondary particulates and with kinetic and mechanistic investigations of the powerful lachrymator peroxybenzoyl nitrate and certain epoxides which demonstrate carcinogenic activity in experimental animals.

Potentially important trace pollutants in synthetic and real atmospheres will be investigated using (1) a unique calibration chamber for determining one atmosphere UV and IR absorption coefficients, (2) a Fourier transform spectrometer installed on the 200-meter LPIR optical system, (3) a combined G.C.-mass spectrometer with photoionization capability for the detection of highly labile species.

C. <u>Related Programs and Activities at the SAPRC</u>

    1. Current Programs

        a. <u>Freon Program</u>. P.I. - Dr. O. C. Taylor. E. I. du Pont de Nemours is currently supporting a program to:

        1) Set up analytical procedures to measure small concentrations of fluorocarbons (Freons) at selected indoor and outdoor sites in the South Coast Air Basin.

        2) Identify the products of photochemical oxidation reactions in both atmospheric and simulated atmospheric environments.

        3) Investigate the effects of these fluorocarbons and their thermal and photochemical decomposition products on vegetation.

        4) Investigate the possible sinks for fluorocarbons emitted into the atmosphere and reactions of these fluorocarbons with such reactive species as $O(^1D)$, OH, and H-atoms.

In the experiments designed to determine plant effects, plants grown in a controlled environment will be exposed to various levels of fluorocarbons. They will be monitored for alterations in their rate of carbon dioxide absorption or emission and inspected for evidence of tissue damage or growth abnormalities.

        b. <u>Aerosol Study</u>. The California Air Resources Board is sponsoring a major campaign to study the different types of aerosols found in various parts of California. Under the management of North American Rockwell Science Center, the investigation will be done by groups from the University of Minnesota, California Institute of Technology, Meteorology Research Incorporated, the California Department of Public Health and the University of California, Riverside.

The objective of this study is to characterize aerosols in terms of their physical and chemical properties, and in terms of their interaction with other pollutants. Identification of aerosol sources, as well as sources of reactive gaseous pollutants which can be related to aerosol pollution and loss of visibility is also intended. Aerosol measurements will be made at three fixed stations in San Jose, Pasadena, and Riverside, and at several other locations with a mobile laboratory. Gaseous pollutant measurements and meteorological data will also be obtained and all data computerized.

The Statewide Air Pollution Research Center participates in the aerosol study in two ways:

        1) By providing a fixed site for short-term, intensive, aerosol measurements using the complete array of particle measuring instruments, along with various gas analysis techniques;

        2) By contributing the specialized techniques which have been developed at the University of California, Riverside for analysis of polluted air to the overall project. These include analysis for PAN, individual hydrocarbons, and aerosol infrared spectra.

c. <u>Analysis of Peroxybenzoyl Nitrate in Photochemical Smog</u>. P.I. – Dr. E. R. Stephens. Funded by California Air Resources Board through PCA.

Peroxybenzoyl nitrate (PBzN) is reported to be eye irritating at concentrations of 5 ppb and is said to be formed by "sunlite" irradiation of various hydrocarbon/nitrogen oxide mixtures which are emitted by various sources in urban areas. Its concentration in real smog has never been measured. Under Project Clean Air a beginning was made on development of a chromatographic method for the quantitative analysis of Riverside smog for PBzN at the ppb level. The general objective is to develop a method for measuring PBzN in ambient air at the 1 to 5 ppb level. Since electron capture chromatography is routinely used to measure the better known homologue PAN in ambient air and since PBzN has been measured by this technique in laboratory mixtures, it is planned to use this technique. When a suitable procedure has been perfected, measurements will be made in various southern California areas to establish typical concentrations of PBzN. This will permit an evaluation of the role of PBzN in causing ambient eye irritation. If it seems necessary, a reevaluation of the PBzN levels necessary to cause eye irritation will be undertaken during the later stages of the project.

d. <u>Formation of Photochemical Aerosols</u>. P. I. – Dr. E. R. Stephens. Funded by EPA.

The aim of this project is to achieve a quantitative understanding of the aerosol component of Riverside smog as a prime example of photochemical smog. We want to determine how much of it is generated by atmospheric chemical reactions and how much is directly emitted by man-made or natural sources. The chemical nature of the processes which produce aerosol and the chemical composition of the resultant aerosols are specific objectives. This will be done by comparing aerosols generated synthetically with those found in Riverside ambient air. Two major techniques will be used: 1) impaction followed by infrared and other types of analysis, and 2) particle sizing and counting using a light scattering counter and pulse height analyzer.

The present project has several special features: 1) emphasis on the chemistry of aerosols rather than their physical and optical properties; the impaction/infrared technique represents an important advance in this study; 2) comparison of the synthetic aerosols with those in photochemical smog; few places are as well located as Riverside for such a comparison; 3) ability to measure other components of smog (such as hydrocarbons and PAN) along with aerosol.

Perhaps the most controversial question to be studied in this program is the importance of photochemically generated <u>organic</u> aerosol as compared to sulfuric acid aerosol (also generated photochemically). Our past results indicating that the latter is an important cause of visibility degradation, while the organic aerosol is a minor factor, are not universally accepted. This has an important bearing on actions to be taken with respect to control of emissions of sulfur dioxide, hydrocarbons, and nitrogen oxides.

The origin of the "nitrate" bands in our aerosol spectra also needs to be clarified. There is some evidence that these bands are present in unreacted (but polluted) air. This needs to be confirmed and explained if the role of

nitrogen compounds is to be clarified.

e. Studies of Hydrocarbons in Ambient Air. P. I. - Dr. E. R. Stephens. Funded by Coordinating Research Council.

The two basic objectives of this project are:

1) To obtain information on the extent to which various individual hydrocarbons and classes of hydrocarbons react to form photochemical air pollution. This is done on actual samples of polluted ambient air as well as laboratory mixtures.

2) To evaluate and use air analysis for hydrocarbons as a method for tracing sources of hydrocarbon pollution.

f. CHESS - Community Health and Environmental Surveillance Studies. P. I. - Dr. C. R. Thompson. Funded by EPA.

The CHESS program for the South Coast Basin is being undertaken by UCR in parallel with similar, ongoing studies in four other urban areas: New York, Salt Lake City, Birmingham, and Chattanooga. The air quality and health effects data which are collected by the UCR team are analyzed by EPA. This epidemiological study includes extensive measurements of air pollutants in seven South Coast Air Basin communities with varying levels of photochemical smog (high, intermediate, and low oxidant levels) coupled with comprehensive surveys of families of school children for indications of respiratory and pulmonary afflictions. These surveys will be conducted for a period of from three to five years. Depending on the kind of health data being collected (e.g., incidence of acute respiratory disease, measurement of pulmonary function, etc.), from 300 to 6000 individuals are included in the survey. Study communities within each geographical region have been carefully matched for climatic and population characteristics so that the major difference among them is in the amount and kind of dominant pollutant to which the people are exposed.

2. Proposed Program

a. Determination of the Spectral Distribution of Absorption Cross Section of Aerosols in Polluted Atmospheres in the Infrared, Visible and New Ultraviolet Regions. P. I. - Dr. George Doyle. Funding sought from EPA.

The overall objective of this project is to obtain data on the volumetric absorption cross-section of anthropogenic atmospheric aerosol in the infrared, visible, and near ultraviolet regions of the spectrum. Such data will facilitate more precise estimation of the climatic effects due to aerosols on the radiation balance of Earth and on the kinetics of cloud formation, and the in situ chemical identification of aerosol materials. These deductions in turn will become part of the scientific basis for setting emission standards and control strategies for particulate (both primary and secondary). In addition, such data will contribute to basic scientific knowledge and technique.

V. BUDGET

Salaries and Wages	Rate[*]	% Time	Cost
Chamber Staff			
Pitts, J. N., Professor VI	$		$ -0-
Winer, A. M., Asst. Res. Chem. III	14,600	40	6,161
Bekowies, P. J., Asst. Res. Chem. III	14,600	40	6,161
McAfee, J., Asst. Res. Chem. I	13,000	50	6,858
Doyle, G. J., Assoc. Res. Chem. IV	20,300	15	3,213
Long, W., Staff Res. Assoc. III-1	10,716	50	6,054
Harris, S., Staff Res. Assoc. I-1½	8,604	50	4,862
Secretary I(SH)-2	6,420	40	2,902
Technology Assessment Staff			
Lloyd, A. C., Asst. Res. Chem. III	14,600	20	3,081
Kuby, W. C., Assoc. Prof. III			-0-
Poe, Minn, Programmer I	11,796	33 1/3	4,443
In-House Support Staff			
Stephens, E. R., Prof. IV			-0-
Atkinson, R., Asst. Res. Chem. II			-0-
Darnall, K., Asst. Res. Chem. III			-0-
Peters, J., Asst. Res. Chem. I			-0-
Wendschuh, P., Asst. Res. Chem. I			-0-

Total Salaries and Wages	$ 43,735

Employee Benefits

Faculty, 15% ($25,474)	3,821	
Staff, 12% (18,261)	2,191	6,012

Permanent Equipment

Beckman Model 6800 (w/recorder) CO, Methane, Total Hydrocarbon Analyzer	9,500	
Data Manager	8,190	
Teletype Interface	1,050	
x-y Plotter	1,103	19,843

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[*]Rates computed at 5.5% increase for faculty and 13% for staff.

V. Budget (continued)

Expendable Equipment & Supplies

Liquid nitrogen	2,810	
Titanium	460	
Electrical power	1,600	
Actinometry supplies and filters	1,000	
Special compressed gas mixtures	3,000	
Miscellaneous (gases, chemicals, pure air system maintenance, hardware, etc.)	3,500	
25 KW Xenon lamp	2,500	14,870

Travel

10 trips to ARB Laboratory, El Monte, at $9.50/trip	95	
2 trips to Sacramento for P.I. and two staff persons at $77/person/trip	462	557

Publications

Report preparation, illustrator, page charges, reprint charges, etc.	2,500

Other Costs

Computer time, including key punching and plotting, 15 hrs. at $225/hr.	3,375	
Instrument maintenance and repair	2,500	5,875

Total Direct Costs	93,392
Total Indirect Costs, at 46% of S&W	20,118
TOTAL BUDGET	$113,510

VI. CURRICULUM VITAE

CHAMBER STAFF

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: James N. Pitts, Jr., Director Statewide Air Pollution Research Center; Professor of Chemistry; Director, TITLE Project Clean Air	SOCIAL SECURITY NO.: 551-22-9719	BIRTHDATE: (Mo., Day, Yr.) Jan. 10, 1921

PLACE OF BIRTH (City, State, Country) Salt Lake City, Utah, U.S.A.	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.) U.S.

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
University of California, Los Angeles	B. S.	1945	Photochemistry and Photochemical Air Pollution
Northwestern University	None	1945-46	
University of California Los Angeles	Ph.D.	1949	

HONORS: Phi Beta Kappa (1945); Guggenheim Fellow, Oxford University, Oxford, England (1960-61); Visiting Research Fellow, Merton College, Oxford University (1965); UC Riverside, Faculty Research Lecturer (1965-66); National Sigma Xi Lecturer (1972-73)

MAJOR RESEARCH INTEREST: Photochemistry and Photooxidations and their Application to Chemistry of Polluted Urban Atmospheres	ROLE IN PROPOSED PROJECT: Principal Investigator

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

Director, Statewide Air Pollution Research Center, Univ. of Calif., 1970-present; Professor of Chemistry, UCR, 1959-present; Director, Project Clean Air, Univ. of Calif., 1971-present; Research Assistant, Div. 10, National Defense Research Committee, OSRD, 1942-1945; Research Associate, Special Projects Div., U.S. Army, 1945-46; Instructor and Assistant Prof. of Chemistry, Northwestern University, 1949-54; Associate Prof. of Chemistry, UCR, 1954-59; Chairman, Dept. of Chemistry, UCR, 1961-63; Academic Advisor to the Chancellor, UC Santa Cruz, 1962-63; Adjunct Faculty Member, Office of Manpower Development, EPA, 1971-present.

Professional Memberships: American Chemical Society, Faraday Society, Sigma Xi, Alpha Chi Sigma, Phi Lambda Upsilon, American Physical Society, Air Pollution Control Assn.

Committees, Editorial Boards, and Conferences: Protective Committee, Advisory Council Army Chemical Corps, 1957-64; Air Pollution Research Grants Advisory Committee, NAPCA, 1964-68; Advisory Board on Military Personnel Supplies, Committee on Textile Functioning Finishing, National Academy of Sciences (NAS), National Research Council (NRC), 1966-71; Technical and Scientific Advisory Committee, California Air Resources Board, 1967-72; Air Pollution Chemistry and Advisory Committee, EPA, 1969-72; Committee on Biological Effects of Atmospheric Pollutants, NAS-NRC, 1970-present; Committee on Kinetics of Chemical Reactions, NAS-NRC, 1970-present; Chairman, Panel on Polycyclic Organic Matter, NAS-NRC; Associate Editor, Panel on Vapor Phase Organic Matter, NAS-NRC, 1972-present; Board of Directors of Pacific Southwest Universities Air Pollution Assn., 1971-present; Co-chairman, Second International IUPAC Symposium on Photochemistry, Enschede, Holland, July 1967; Chairman, 1973 Gordon Research Conference on Environmental Sciences, Air; Editorial Advisory Boards of Journal of Environmental Science and Technology, Environmental Letters, and Chemosphere.

James N. Pitts, Jr. (Continued)

Publications: Author of approximately 110 scientific articles
on photochemistry, air pollution, and related subjects. Coauthor, with J. G.
Calvert, Photochemistry, John Wiley & Sons, 1966; Coauthor, Graduate School in the
Sciences: Entrance, Survival and Careers (with J. G. Calvert and G. H. Dorion),
John Wiley & Sons, 1972; Coeditor, Advances in Photochemistry, volumes 1-8 (with
W. A. Noyes, Jr. and G. S. Hammond and K. Gollnick and G. S. Hammond) Wiley-
Interscience; Coeditor, Advances in Environmental Science and Technology, volumes
1 and 2; Coeditor, Monographs and Texts in Environmental Science and Technology
(with R. L. Metcalf) Wiley-Interscience; Coeditor, Annual Survey of Photochemistry,
1967 and 1968 (with N. J. Turro, D. Valentine, Jr., and G. S. Hammond).

Selected Invited Scientific Lectures

Chemiluminescent Reactions of Ozone with Olefins and Organic Sulfides
     International Symposium on Identification and Measurement of Environmental
     Pollutants, Ottawa, Ontario, Canada, June 14, 1971
The Photochemistry of Urban Atmospheres
     Eleventh Latin American Congress in Chemistry
     Santiago, Chile, January 5-11, 1972
Some Social and Chemical Aspects of Air Pollution
     Twenty-fourth E. C. Franklin Memorial Lecture, Alpha Rho Chapter of ΦΛΤ
     University of Kansas, Lawrence, April 19, 1972
Physical Organic Chemistry in the Environmental Sciences: Challenge in Air
     Pollution, First IUPAC Conference on Physical Organic Chemistry
     Crans-sur-Sierre, Switzerland, September 4-8, 1972
Photochemical Air Pollution: Challenge to Science and to Society
     Symposium on Photochemical and Photophysical Processes
     University of Texas, November 1972

Selected Publications: Symposia and Chapters

Photochemical Air Pollution: Singlet Molecular Oxygen as an Environmental Oxidant
     J. N. Pitts, Jr.; Advances in Environmental Sciences, Vol. I, John Wiley &
     Sons, Inc., New York, 1969, pp. 289-337, edited by J. N. Pitts, Jr. and
     R. L. Metcalf
Modeling, A Fundamental Problem of Pollution Control
     J. N. Pitts, Jr.; Cybernetics and the Management of Large Systems, Spartan
     Books, New York, 1969, pp. 217-243.
Environmental Appraisal: Oxidants, Hydrocarbons, and Oxides of Nitrogen
     J. N. Pitts, Jr.; APCA Symposium Proceedings, J. Air Poll. Cont. Assoc., 19, 658 (1969)
Some Fundamental Aspects of Photochemistry and Photochemical Air Pollution
     J. N. Pitts, Jr.; Combustion Generated Air Pollution, edited by E. S. Starkman,
     Plenum Publishing Corp., New York, 1971
The Role of Singlet Molecular Oxygen in the Chemistry of Urban Atmospheres
     J. N. Pitts, Jr.; Chemical Reactions in Urban Atmospheres, edited by C. S.
     Tuesday, American Elsevier Publishing Co., Inc., 1971
Environmental Implications of a National Material Policy: Air Pollution - A Case
     Study, J. N. Pitts, Jr. and A. C. Lloyd; Report of the UCLA Forum on National
     Materials Policy, Chairman, A. S. Tetelman, June 1972
Photochemical Smog
     Proceedings, International Symposium on Air Pollution, Tokyo, 1972,
     October 1972, J. N. Pitts, Jr. and G. E. Grimstone, pp.41-60.

James N. Pitts, Jr. (Continued)

Selected Research Papers

On the Stability of Acrolein towards Photooxidation in the Near Ultraviolet,
    Int. J. Air Water Poll., 6, 1, (1962), A. D. Osborne,
    J. N. Pitts, Jr. and E. F. Darley
Effects of Wavelength and Temperature on the Primary Processes of Nitrogen Dioxide
    and a Spectroscopic-Photochemical Determination of the Dissociation Energy,
    J. Chem. Phys., 40, 3655 (1964), J. N. Pitts, Jr., J. H. Sharp, and S. I. Chan
A Rapid Actinometer for Photochemical Air Pollution Studies, Intern. J. Air
    Water Poll., 9, 595 (1965), J. N. Pitts, Jr., J. M. Vernon, and J. K. S. Wan
Relationships between Certain Meteorological Factors and Photochemical Smog, Intern.
    J. Air Water Poll., 10, 689 (1966), E. A. Schuck, J. N. Pitts, Jr.,
    and J. K. S. Wan
Singlet Oxygen in the Environmental Sciences. I. The Role of Singlet Molecular
    Oxygen in the Production of Photochemical Air Pollution, Environ. Sci. Technol.,
    1, 656 (1967), A. U. Khan, J. N. Pitts, Jr., and E. B. Smith
A Film Actinometer for the Measurement of Solar Ultraviolet Radiation Intensities
    in Urban Atmospheres, Environ. Sci. Technol., 2, 435 (1968), J. N. Pitts, Jr.,
    G. W. Cowell, and D. R. Burley
The Base-Induced Decomposition of Peroxyacetyl Nitrate, Tetrahedron Lett., 3765
    (1969), R. P. Steer, K. R. Darnall, and J. N. Pitts, Jr.
Singlet Oxygen in the Environmental Sciences. VIII. Production of $O_2(^1\Delta_g)$ by Energy
    Transfer from excited Benzaldehyde under Simulated Atmospheric Conditions,
    Environ. Sci. Technol., 4, 506 (1970), J. W. Coomber and J. N. Pitts, Jr.
Nitrogen Dioxide Catalyzed Cis-Trans Isomerization of cis-2-Butene, J. Amer. Chem.
    Soc., 93, 4358 (1971), J. L. Sprung, H. Akimoto, and J. N. Pitts, Jr.
Chemiluminescent Reactions of Ozone with Hydrogen Sulphide, Methyl Mercaptan,
    Dimethyl Sulphide and Sulphur Monoxide, Chem. Phys. Lett., 12, 199-202 (1971),
    H. Akimoto, B. J. Finlayson, and J. N. Pitts, Jr.
Production of Vibrationally Excited OH in Chemiluminescent Ozone-Olefin Reactions,
    Chem. Phys. Lett., 12, 495 (1972), B. J. Finlayson, J. N. Pitts, Jr., and
    H. Akimoto
Chemiluminescent Reactions of Peroxyacetyl Nitrate and Ozone with Triethylamine.
    A Possible Atmospheric Monitor for Peroxyacetyl Nitrate, . Environ. Sci.
    Technol., 7, 000 (1973), J. N. Pitts, Jr., H. Fuhr, J. Gaffney, J. Peters

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: Arthur M. Winer	SOCIAL SECURITY NO.:	BIRTHDATE: (Mo., Day, Yr.)
TITLE Assistant Research Chemist	573-64-7576	May 5, 1942
PLACE OF BIRTH (City, State, Country) New York City, New York, U.S.A.	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.) U.S.	

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
University of California Los Angeles	B.S.	1964	Chemistry
The Ohio State University	Ph.D.	1969	Physical Chemistry

HONORS: Continental Oil Graduate Fellow, OSU, 1968-69; Gulf Graduate Fellow in Physical Chemistry, OSU, 1967-68; National Science Foundation Undergraduate Research Participant, UCLA, 1964; Honors at Entrance, UCLA, 1960.

MAJOR RESEARCH INTEREST: Chemistry and physics of air pollution, gas phase kinetics, IR & EPR spectroscopy, applied laser research

ROLE IN PROPOSED PROJECT: Co-Investigator

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1972-present — Project Manager, Smog Chamber Facility, and Assistant Research Chemist, Statewide Air Pollution Research Center, University of California, Riverside.

1971-1972 — Assistant Research Chemist, Department of Chemistry and Statewide Air Pollution Research Center, University of California, Riverside. Fundamental and applied studies in photochemistry and photochemical air pollution using long-path infrared and electron paramagnetic resonance spectroscopies. Member of team responsible for design and fabrication of SAPRC smog chambers and solar simulator.

1970-1971 — Postdoctoral Fellow, Department of Chemistry, University of California, Berkeley, with Professor G. C. Pimentel. Ultra-rapid scan infrared spectroscopy of free radicals. First infrared detection of CH_3 and its deuterium isotopes in the gas phase. Analysis and interpretation of Mariner VI and VII infrared data by atmosphere simulation studies using a 2.5 km path length IR cell. Investigation of stimulated emission from polyatomic molecules and radicals (chemical lasers).

1964-1969 — Graduate Student and Graduate Fellow, Department of Chemistry, The Ohio State University, Columbus, Ohio, with Professor R. E. Gerkin. Electron paramagnetic resonance (EPR) studies of the phosphorescent state of oriented aromatic hydrocarbons in single crystals at low magnetic fields. Very precise determination of zero-field splitting (ZFS). Observation by EPR of multiple orientation of guest molecules in organic mixed crystals. Measurement and interpretation of the temperature dependence of ZFS and triplet state lifetimes in such crystals. First unambiguous observation of a deuterium isotope effect in ZFS.

Arthur M. Winer (Continued)--pg. 2

1964	National Science Foundation Undergraduate Research Participant, University of California, Los Angeles, with Professor K. D. Bayes. Investigation of the rate of deactivation of metastable singlet oxygen, $O_2(a^1\Delta)$, due to collision with ground-state oxygen. First gas phase reaction of singlet oxygen with an olefin.
1962-1964	Part-time Laboratory Assistant, Korad Corporation, Santa Monica, California. Spectrophotometric and quantitative analysis of laser boule materials. Purification of nitrobenzene solutions for use in Q-switching Kerr cells. Growth of ruby laser boules and doped alkali-halide single crystals (potential laser systems) by the Vernueil and Czochralski methods, respectively.

<u>Professional Memberships</u>: American Institute of Physics; Optical Society of America; American Chemical Society; American Association for the Advancement of Science; Coblentz Society.

Arthur M. Winer (Continued)

<u>Publications</u>

The Decay of O_2 $(a^1\Delta)$ in Flow Experiments
    J. Phys. Chem., <u>70</u>, 302 (1966)
    A. M. Winer and K. D. Bayes

Observation of Multiplet Structure in Low-field Magnetic Resonance Spectra
of Triplet States of Oriented Aromatic Hydrocarbons
    J. Chem. Phys., <u>47</u>, 2504 (1967)
    R. E. Gerkin and A. M. Winer

Deuterium Isotope Effect in Zero-field Splittings of Phosphorescent
Phenanthrene Oriented In Biphenyl
    J. Chem. Phys., <u>50</u>, 3114 (1969)
    R. E. Gerkin and A. M. Winer

Proton Hyperfine Structure at Magnetic Fields Below ~100 G in Electron
Magnetic Resonance Absorptions by Triplet States of Aromatic Molecules
    J. Chem. Phys., <u>51</u>, 1664 (1969)
    R. E. Gerkin and A. M. Winer

Electron Paramagnetic Resonance Absorption in Oriented Phosphorescent Chrysene
at Magnetic Fields Below 125 G. I. Multiplet Structure in Low-field Spectra
    J. Chem. Phys., <u>56</u>, 1359 (1972)
    R. E. Gerkin and A. M. Winer

The Composition of the Martian Atmosphere: Minor Constituents
    Icarus, <u>16</u>, 543 (1972)
    D. Horn, J. M. McAfee, A. M. Winer, K. C. Herr and G. C. Pimentel

Infrared Spectrum of Gaseous Methyl Radical by Rapid-Scan Infrared Spectroscopy
    J. Chem. Phys., <u>57</u>, 4028 (1972)
    L. Y. Tan, A. M. Winer and G. C. Pimentel

Electron Paramagentic Resonance Absorption in Oriented Phosphorescent
Chrysene at Magnetic Fields Below 125 G. II. Multiple Orientation of
Chrysene Triplets in Single Crystals
    J. Chem. Phys., <u>58</u>, 0000 (1973)
    R. E. Gerkin and A. M. Winer

The Photostability of Fluorocarbons
    Submitted to Environmental Science and Technology
    S. Japar, J. N. Pitts, Jr., and A. M. Winer

Deuterium Isotope Effects in Zero-field Splittings of Triplet States of
Oriented Aromatic Hydrocarbons
    To be submitted to the Journal of Chemical Physics
    R. E. Gerkin, D. L. Thorsell and A. M. Winer

Water Vapor in the Martian Atmosphere from Mariner 6 and 7 Infrared Spectra
    In preparation
    J. M. McAfee, A. M. Winer, K. C. Herr and G. C. Pimentel

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: Paul J. Bekowies	SOCIAL SECURITY NO.:	BIRTHDATE: (Mo., Day, Yr.)
TITLE Assistant Research Chemist	478-50-1887	October 2, 1941

PLACE OF BIRTH (City, State, Country)

Detroit, Michigan, U.S.A.

PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.)

U.S.

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
University of Dubuque, Dubuque, Iowa	None	1959-61	Chemistry
University of Minnesota, Minneapolis	B.A.	1963	Chemistry
Cornell University, Ithaca, New York	Ph.D.	1970	Chemistry

HONORS: Honors Scholarship, 1959-60; President's Scholarship, 1960-61; Wahlert Chemistry Scholarship, 1960-61.

MAJOR RESEARCH INTEREST: Photochemistry and EPA studies of air pollutants; Smog chamber studies including analytical chemistry

ROLE IN PROPOSED PROJECT:

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1972-present Assistant Research Chemist, Department of Chemistry and Statewide Air Pollution Research Center, University of California, Riverside. Manages Chamber Analytical Laboratory. Responsible for all analytical instrumentation, data collection and interpretation associated with SAPRC Smog Chambers.

1970-1971 Postgraduate Research Chemist with Professor James N. Pitts, Jr., University of California, Riverside. Carried the major responsibility for design and construction of SAPRC Smog Chamber facility through August 1972. Initiated electron paramagnetic resonance (EPR) studies on gas phase reactions of air pollution interest involving singlet molecular oxygen, and other reactions involving nitrogen oxides. Carried out exploratory studies on the stability of carbon monoxide in air, using long-path infrared spectrophotometry.

1966-1970 Research and Teaching Assistant with Professor A. C. Albrecht, Department of Chemistry, Cornell University, Ithaca, New York. Performed EPR studies to elucidate the nature of trapping sites for photo injection of electrons in polar and non-polar organic glasses at 77°K. Studied benzene anions formed by methods developed above, formed first evidence for the existence of dimeric benzene monoanions. Assisted in laboratory teaching of Honors course in freshman chemistry.

Paul J. Bekowies (continued)

1963-1966   Research Chemist, Eastman Kodak Company, Rochester, New York, with Dr. T. H. James. Performed basic studies on the mechanism of latent image formation in silver halide systems. Designed sophisticated high-vacuum sensitometer for use in studies of latent image formation in photographic films. Studied inter- action of light with silver halide systems as a function of crystal size, shape, oxygen content, and mode of sensitization.

<u>Professional Memberships</u>: American Chemical Society; American Association for Advancement of Science.

Publications

Electron Spin Resonance Studies of Trapped Electrons in Nonpolar Matrices at 77° K
> Ph.D. thesis, Cornell University, June 1971
> Paul John Bekowies

Methyl Radical Formation during Photolysis of N,N,N'N'-Tetramethyl- paraphenylenediamine in 3-Methylpentane at 77° K
> J. Phys. Chem., <u>75</u>, 431 (1971)
> P. J. Bekowies and A. C. Albrecht

Static Interaction of Materials with Ozone at ppm Concentrations
> In preparation
> P. J. Bekowies, J. Gaffney, S. Sheldon and J. N. Pitts, Jr.

Numerous intracompany publications while at the Eastman Kodak Company. Individual titles cannot be listed because they are classified information.

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: John M. McAfee	SOCIAL SECURITY NO.:	BIRTHDATE: (Mo., Day, Yr.)
TITLE Postdoctoral Research Chemist	564-76-6939	October 9, 1946
PLACE OF BIRTH (City, State, Country) Santa Monica, California, U.S.A.	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.) U.S.	

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
San Jose State College, San Jose	B.S.	1968	Chemistry
University of California, Berkeley	Ph.D.	1972	Physical Chemistry

HONORS: Departmental Award in Chemistry, San Jose State College; Standard Oil Fellowship 1970-71, University of California, Berkeley.

MAJOR RESEARCH INTEREST: Spectroscopy of planetary atmospheres: infrared absorption spectroscopy, atmospheric chemistry.	ROLE IN PROPOSED PROJECT: Assistant Research Chemist

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1972-present	Postdoctoral Research Chemist, Statewide Air Pollution Research Center, University of California, Riverside.
1968-1972	Research Assistant, Department of Chemistry, University of California, Berkeley. Used quantitative infrared spectroscopy at long (2.5 km) paths and variable temperatures (185 to 300°K) to spectroscopically simulate the Martian atmosphere. A considerable amount of time was spent on absorption band models and interpreting the Mariner 6 and 7 infrared spectrometer data as it applied to the atmosphere of Mars. Results obtained include the most reliable measurement of the CO_2 abundance, topographic variation of the surface, a measurement of the H_2O abundance and temperature, and an upper limit on some 30 compounds of possible interest in the chemistry of the Martian atmosphere.
1967-1968	Research Technician-Chemist, Lawrence Livermore Labs, Livermore, California. Measured transport properties of radioactive ions in acid solution under special electrochemical conditions. Dealt with computer programs for determination of alpha decay spectra.
1966-1967	Research Technician, San Jose State Foundation, San Jose State College, San Jose, California. Developed quantitative C^{14} tracer techniques for determination of Si analog drugs in laboratory animals.

John M. McAfee (Continued)

Publications

Martian Topography from the Mariner 6 and 7 Infrared Spectra
    Astron. J., 75, 883 (1970)
    K. C. Herr, D. Horn, J. M. McAfee and G. C. Pimentel

The Composition of the Martian Atmosphere: Minor Constituents
    Icarus, 16, 543 (1972)
    D. Horn, J. M. McAfee, A. M. Winer, K. C. Herr and G. C. Pimentel

Water Vapor in the Martian Atmosphere from Mariner 6 and 7 Infrared Spectra
    In preparation
    J. M. McAfee, A. M. Winer, K. C. Herr and G. C. Pimentel

An Infrared Measurement of the CO Abundance on Mars
    In preparation
    J. M. McAfee, D. Horn, K. C. Herr and G. C. Pimentel

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: George J. Doyle	SOCIAL SECURITY NO.:	BIRTHDATE: (Mo., Day, Yr.)
TITLE Associate Research Chemist	568-48-8938	August 4, 1918

PLACE OF BIRTH (City, State, Country)	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.)
San Jose, California, U.S.A.	U.S.

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
San Jose State College, San Jose, California	B.A.	1940	Chemistry, Liberal Arts
California Institute of Technology, Pasadena, Calif.	M.S.	1947	Physical Chemistry
Indiana University, Bloomington, Indiana	Ph.D.	1955	Physical Chemistry

HONORS:

MAJOR RESEARCH INTEREST: Physics and chemistry of aerosols and their role in air pollution	ROLE IN PROPOSED PROJECT: Co-investigator

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1971-present Associate Research Chemist, Statewide Air Pollution Research Center, University of California, Riverside. Designed and oversaw construction of air purification system and conventional chamber at the Center's chamber facility. At present initiating a program of study and research on aerosols in polluted atmospheres.

1954-1971 Physical Chemist to Senior Physical Chemist, Stanford Research Institute, Pasadena, California. A variety of research jobs typical of a contract-research organization. These included pioneering research on the reactions of nitrogen oxides and ozone at trace concentrations, studies of rates and stoichrometry of photooxidations of olefins in air as sensitized by nitrogen oxides, studies of auto exhaust photooxidations, and research on the formation of aerosols in similar mixtures, particularly in the presence of traces of sulfur dioxide. Designed a smog chamber and air purification system. Also included studies of the reactions and fates of sulfur compounds in natural gas distribution systems and studies of the light scattering properties of cotton fibers and their agglomerates directed towards the design of cotton quality control instrumentation. Carried out a preliminary study on the possible use of clustering on thermionically generated lithium ions to purify space cabin atmospheres.

George J. Doyle (Continued)--pg. 2

1952-1954	Junior Research Chemist, University of California, Berkeley. Work in collaboration with Professor Chester T. O'Konski directed towards studies on the kinetics of self-nucleation and growth of aerosol particles. Major contribution to the design and construction of a light scattering particle size spectrometer and photometer to be used in these studies. This instrument later served as a prototype for the Royco particle counters. Some preliminary studies of sulfur aerosol formation from flash photolysis of hydrogen sulfide.
1947-1952	Research Associate, Indiana University, Indiana. Physics and chemistry of aerosols under the direction of Dr. Frank T. Gucker and directed towards the publication of a Ph.D. thesis on the interaction of sound and aerosol particles. Involved the construction of aerosol generators, sedimentation cells, and a special precision sound generator in order to obtain data on the relationship between particle size and motion in a well characterized sound field.
1945-1946	Research Assistant, California Institute of Technology. War-related research under auspices of the NDRC. Mechanical properties and chemical analyses of rocket propellants with emphasis on ballistite-like compositions.
1942-1945	Research Assistant, Northwestern University, Evanston, Illinois. War-related research under auspices of the NDRC. Research on gas adsorption by gas-mask charcoals and the efficacy of catalysts on charcoal carriers. Studies of use of non-persistant war gases in the field.

Professional Memeberships: Sigma Xi; Phi Lambda Upsilon; American Physical Society; American Chemical Society.

Committees: American Society for Testing Materials, Committee D-22 (1968-69).

G. J. Doyle (Continued)

Publications

Molecular Properties of Nitrocellulose (I) Studies of Viscosity
    J. Phys. Colloid Chem., 51, 569 (1947)
    G. J. Doyle, G. Herbottle, R. M. Badget and R. M. Noyes

Viscoelastic Behavior of a Highly Plasticized Nitrocellulose in Compression
Under Constant Load
    J. Appl. Phys., 19, 373 (1948)
    G. J. Doyle and R. M. Badger

Kinetics of the Acid Catalyzed Hydrolysis of Amine Disulfonate Ion-Third
Ionization Constant of Amine Disulfonic Acid
    J. Amer. Chem. Soc., 71, 3491 (1949)
    G. J. Doyle and N. J. Davidson

Retentivity of Charcoals-effect of Moisture on the Retentivity for Methyl
Ethyl Ether, Neopentane and Methanol
    J. Phys. Chem., 56, 182 (1952)
    D. H. Volman and G. J. Doyle

Light Scattering Studies in Aerosols with a Counter-Photometer
    Anal. Chem., 27, 694 (1955)
    C. T. O'Konski and G. J. Doyle

Sonic Determination of Particle Size in Aerosols
    Univ. Microfilms Publ. No. 14658, 18 pp of Dissertation Abstracts, 16,
    Z48 (1956)
    G. J. Doyle

Amplitude of Vibration of Aerosol Droplets in a Sonic Field
    J. Phys. Chem., 60, 989 (1956)
    F. T. Gucker and G. J. Doyle

Rate Constants at Low Concentrations. I Rate of Reaction of O_3 with NO_2
    J. Chem. Phys., 26, 1336 (1957)
    H. W. Ford, G. J. Doyle and N. Endow

Rate Constants at Low Concentrations. II Reaction between Nitric Oxide and
Ozone in Air at Room Temperature
    J. Chem. Phys., 26, 1337 (1957)
    H. W. Ford, G. J. Doyle and N. Endow

Formation of Aerosols by Irradiation of Dilute Auto Exhaust
    J. Air Poll. Control Assoc., 8, 23 (1958)
    G. J. Doyle and N. A. Renzetti

Nature of the Particulate in Irradiated Automobile Exhaust
    Air Poll. Control Assoc., 8, 293 (1959)
    N. A. Renzetti and G. J. Doyle

G. J. Doyle (Continued)

Publications (Continued)

Photoxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen
and Sulfur Dioxide
    Air Pollution Foundation Report, 29, 110 pp (1959); CA 54, 4119f, (1960);
    also CA 51, 9048b
    E. A. Schuck and G. J. Doyle

Kinetics of Photolysis of Low Concentrations of Nitrogen Dioxide in Air
    Advances Chem. Ser., 21, 410 (1959); CA 54, 4120a (1960)
    H. W. Ford, G. J. Doyle and N. Endow

Photochemical Aerosol Formation in Sulfur Dioxide Hydrocarbon Systems
    Intern. J. Air Poll., 2, 327 (1960)
    N. A. Renzetti and G. J. Doyle

Rate Constants at Low Concentrations. V. Mechanism of Reaction of Ozone with
Photolyzing Nitrogen Dioxide in Presence of Excess Oxygen
    J. Chem. Phys., 32, 1256 (1960); CA 51 14386h
    H. W. Ford, G. J. Doyle and N. Endow

Self-nucleation in the Sulfuric Acid-Water System
    J. Chem. Phys., 35, 795 (1961); See also "Chemical Reactions in the
    Lower and Upper Atmosphere," Interscience, 1961, p. 87
    G. J. Doyle

Sulfur Dioxide Role in Eye Irritation
    Arch. Environ. Health, 3, 657 (1961); CA 56, 76466
    G. J. Doyle, N. Endow and J. L. Jones

Nature of Some Model Photochemical Aerosols
    J. Air Poll. Control Assoc., 13, 141 (1963); CA 59, 1216e
    N. Endow, G. J. Doyle and J. L. Jones

Automobile Exhaust - Gas Aerosols: A Review of Studies Conducted at Stanford
Research Institute
    J. Air Poll. Control Assoc., 13, 365 (1963)
    G. J. Doyle and J. L. Jones

Design of a Facility (Smog Chamber) for Studying Photochemical Reactions
under Simulated Tropospheric Conditions
    Env. Sci. Technol., 4, 907 (1970)
    G. J. Doyle

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: William Long	SOCIAL SECURITY NO.:	BIRTHDATE: (Mo., Day, Yr.)
TITLE Staff Research Associate	166-36-5909	Oct. 12, 1944

PLACE OF BIRTH (City, State, Country)	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.)
Bedford County, Pennsylvania, U.S.A.	U.S.

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
Pennsylvania State University	Associate	1965	Electrical and Electronics Technology

HONORS:

MAJOR RESEARCH INTEREST: Aerosol generation and particulate sampling	ROLE IN PROPOSED PROJECT:

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1970-present   Staff Research Associate, Statewide Air Pollution Research Center, University of California, Riverside.

1969-1970   Lab Technician, Environmental Research Corporation, St. Paul, Minnesota. Worked on research program for development of aerosol inhalers for respiratory use. Determined inhaler output aerosol size distribution. Did work on program of comparing various methods of particulate sampling (aerosol size distribution) in different types of industrial environments. Worked with odorous pollutant sampling and odor scrubbing equipment.

1967-1969   Lab Technician, Statewide Air Pollution Research Center, University of California, Riverside. Aided in establishment of aerosol laboratory. Built spinning disk aerosol generator and fluid atomization aerosol generator used in scrubber tests.

1965-1967   Lab Technician, Pennsylvania State University, Center for Air Environment Studies. Worked on Development of aerosol generation instrumentation. Performed research work on development of Lundgren Inertial Impactor for particulate sampling. Obtained aerosol size and distribution data in study of smoke plume dispersion using fixed wing and a rotary wing aircraft. Aided in the air pollution technician training program.

TECHNOLOGY ASSESSMENT STAFF

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: Alan C. Lloyd	SOCIAL SECURITY NO.:	BIRTHDATE: (Mo., Day, Yr.)
TITLE Assistant Director and Assistant Research Chemist	212-64-8646	Jan. 17, 1942

PLACE OF BIRTH (City, State, Country)	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.)
Milford Haven, Wales	U.K.

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
University College of Wales, Aberystwyth	B.S.	1964	Chemistry
University College of Wales, Aberystwyth	Ph.D.	1967	Gas Kinetics

HONORS: Visiting scientist, National Bureau of Standards, Washington DC, 1969-1970.

MAJOR RESEARCH INTEREST:	ROLE IN PROPOSED PROJECT:
Gas phase kinetics, free-radical chemistry chemistry of air pollution	Co-investigator

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1972-present Assistant Director, Statewide Air Pollution Research Center and Assistant Research Chemist, Department of Chemistry and Statewide Air Pollution Research Center, University of California, Riverside. Provides technical assistance on atmospheric chemistry and air pollution control to the Director. Coordinated a two-quarter course on "The Nature and Control of Air Pollution."

1970-1971 Postgraduate Research Chemist for Professor James N. Pitts, Jr., Department of Chemistry, University of California, Riverside. Evaluated rate data pertinent to polluted atmospheres. Aided in the design and production of a course in atmospheric chemistry given by Professor Pitts.

1969-1970 Visiting Scientist, U.S. Department of Commerce, National Bureau of Standards; working with Dr. David Garvin. Performed critical evaluations of gas kinetic data for (1) dissociation-recombination reactions of fluorine and chlorine and (2) the reactions of the hydroperoxyl radical. Assisted in the day to day operations of the Kinetics Data Center and in answering requests for information on kinetic data.

1967-1969 Office for Scientific and Technical Information Research Fellow, Department of Chemistry, University of Leeds, Leeds, England. Participated in the initiation of a program designed to produce a compilation of critically evaluated kinetic data for reactions of interest in high temperature processes. The results of the evaluations were published as reports on a continuing basis. Performed studies on experimental determinations of rate data for reactions of the trifluoromethyl radical with ammonia and hydrazine.

Alan C. Lloyd (Continued)--pg. 2

Professional Memberships: Member of the Chemical Society; American Association for the Advancement of Science.

Review Panel: Participating in the compilation of reliable rate data for reactions of stratospheric interest being coordinated by Professor H. Johnston, University of California, Berkeley, and Dr. David Garvin, National Bureau of Standards, Washington DC.

Publications:

Hydrogen-abstraction Reactions by Methyl Radicals from Nitrogen-Containing Compounds
      J. Chem. Soc. (A), 621 (1966)
      D. A. Edwards, J. A. Kerr, A. C. Lloyd, and A. F. Trotman-Dickenson

Hydrogen-abstraction Reactions by Ethyl Radicals from Methylamines and Hydrazine
      J. Chem. Soc. (A), 1500 (1966)
      D. A. Edwards, J. A. Kerr, A. C. Lloyd, and A. F. Trotman-Dickenson

Kinetics of the Decomposition of the Propionyl Radical
      Chem. Commun., 164 (1967)
      J. A. Kerr and A. C. Lloyd

Kinetics and Pressure Dependence of the Decomposition of the Propionyl Radical
      Trans. Faraday Soc., 63, 2480 (1967)
      J. A. Kerr and A. C. Lloyd

Decomposition Reactions of Radicals
      Quart. Revs., 22, 549 (1968)
      J. A. Kerr and A. C. Lloyd

Tables of Conversion Factors for Reaction Rate Constants
      J. Chem. Ed., 46 54 (1969)
      D. D. Drysdale and A. C. Lloyd

Attack of Trifluoromethyl Radicals on Ammonia and Ammonia-d_3
      Trans. Faraday Soc., 65, 775 (1969)
      N. L. Arthur, P. Gray, and A. C. Lloyd

High Temperature Reaction Rate Data No. 1
      May 1968
      D. L. Baulch, D. D. Drysdale, and A. C. Lloyd

High Temperature Reaction Rate Data No. 2
      November 1968
      D. L. Baulch, D. D. Drysdale, and A. C. Lloyd

High Temperature Reaction Rate Data No. 3
      April 1969
      D. L. Baulch, D. D. Drysdale, and A. C. Lloyd

Alan C. Lloyd (Continued)--pg. 3

High Temperature Reaction Rate Data No. 4
    March 1970
    D. L. Baulch, D. D. Drysdale, D. G. Horne, andA. C. Lloyd

Reactions of the Hydroxyl Radical in the Gas Phase
    Oxidation and Combustion Reviews, 4, 157 (1970)
    D. D. Drysdale and A. C. Lloyd

A Critical Review of the Dissociation-Recombination Reactions of Fluorine and
Chlorine
    Int. J. Chem. Kinetics, 3, 39 (1971)

Estimated and Evaluated Kinetic Data for Gas Phase Reactions of the Hydro-
peroxyl Radical
    N.B.S. Report 10447, July 1971; Int. J. Chem. Kinetics [in press] (1972)
    A. C. Lloyd

Evaluated Kinetic Data for High Temperature Reactions
    Vol. I. Butterworths, London (1972)
    D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd

Environmental Implications of a National Material Policy: Air Pollution - A
Case Study
    Report of the UCLA Forum on National Materials Policy, Chairman, A. S.
    Tetelman, June 1972
    J. N. Pitts, Jr. and A. C. Lloyd

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: William C. Kuby	SOCIAL SECURITY NO.:	BIRTHDATE: (Mo., Day, Yr.)
TITLE Associate Professor of Mechanical Engineering	350-26-2334	Oct. 21, 1932

PLACE OF BIRTH (City, State, Country)	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.)
Oak Park, Illinois, U.S.A.	U.S.

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
Northwestern University Evanston, Illinois	B.S.	1955	Chem. Engineering
Northwestern University Evanston, Illinois	M.S.	1957	Chem. Engineering
Northwestern University Evanston, Illinois	Ph.D.	1960	Chem. Engineering

HONORS: Murphy Scholar, Dow Fellow, Union Carbide Fellow, Tau Beta Pi (Engineering)

MAJOR RESEARCH INTEREST: Fluid mechanics, chemical kinetics, air pollution	ROLE IN PROPOSED PROJECT:

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

| 1966-present | Associate Professor of Mechanical Engineering, Associate Dean, College of Engineering, University of California, Santa Barbara |
| 1961-1966 | Aeronutronic, Philco-Ford, Supervisor, Real Fluids Section |

Professional Societies: Member, Sigma Xi (Research); Phi Lambda Upsilon (Chemistry); AIAA; Combustion Institute

Principal Fields of Interest: Fluid mechanics including real gas effects such as equilibria and chemical and physical kinetics. In particular, shock tube studies related to high temperature gas relaxation phenomena, computer solutions to boundary layer problems in transient thermoanalyses, turbulent effects on chemical reaction kinetics associated with modeling of photochemical smog production and modeling of forest fire propagation. Previous experience includes: heat transfer from two-phase flows; recombination and particle lag effects and performance of ablative materials in solid rocket motor aft-closures and nozzles; reentry solutions for blunt body flows including radiation phenomenon and chemical kinetics.

William C. Kuby (Continued)

Selected Publications

Experimental Investigations of Unstable Burning in Solid Propellant Rocket Motors
    Progress in Astronautics and Rocketry, Vol. 1, Solid Propellant Rocket
    Research (Academic Press, New York, 1960, p. 495-525
    E. M. Landsbaum, W. C. Kuby, and F. W. Spaid

The Internal Environment of a Solid Propellant Rocket Nozzle
    Invited Survey Paper presented at AIAA Solid Propellant Conference, Palo Alto,
    California, January 1962
    W. C. Kuby

The Prediction of Heat Transfer and Ablation in the Aft-Closure of a Solid Pro-
Pellant Rocket Motor
    Trans. of the 7th Symposium on Ballistic Missile Defense, August 1962
    W. C. Kuby and J. L. Richardson

Recent Progress in the Study of Hydrogen Recombination in Nozzle Flows for the
H_2/F_2 System
    Proceedings of the 1st Meeting, Working Group on Thermochemistry, 1963
    W. C. Kuby

Experiments on Hydrogen Recombination in Nozzle Flows for the H_2/F_2 System
    AIAA Journal, 4:160-163 (1966)
    W. C. Kuby

The Use of the Method of Integral Relations for the Determination of the Convective
Heat Flux to a Re-entry Body
    AIAA Journal, 4:947-949 (1966)
    W. C. Kuby

Symmetrical, Equilibrium Flow Past a Blunt Body at Superorbital Re-entry Speeds
    AIAA Journal, 5:610-617 (1967)
    W. C. Kuby, R. M. Foster, S. R. Byron, and M. Holt

Semiempirical Calculations of the Interaction of a Slightly Underexpanded Jet with
a Quiescent Atmosphere
    Journal of Spacecraft and Rockets, Vol. 7, No. 7, July 1970, p. 871-873
    Jose Chirivella and W. C. Kuby

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: Minn Poe TITLE	SOCIAL SECURITY NO.: 104-34-2612	BIRTHDATE: (Mo., Day, Yr.) 9/30/43
PLACE OF BIRTH (City, State, Country) Kweilin, Kwangsi, China	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.) U.S.	

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
University of California, Berkeley	B.S.	1965	Chemistry

HONORS:

Phi Beta Kappa; Iota Sigma Pi

MAJOR RESEARCH INTEREST: Computer simulation modeling of photochemical air pollution; statistical analyses of air pollutant measurements.	ROLE IN PROPOSED PROJECT: Assistant Programmer

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1969-present   Assistant Programmer, Statewide Air Pollution Research Center, University of California, Riverside. Computer simulation modeling of photochemical air pollution; statistical analyses of aerometric data and of air pollution effects on plants; statistical analyses of omissions from fires for burning modeling.

1968-1969   Programmer I, Riverside School Study, University of California, Riverside. Processing and programming statistical analyses for sociological data collected from desegregation studies.

1965-1967   Laboratory Technician I, Horticultural Science Department, University of California, Riverside. Testing effects of herbicides on rates of protein and lipid syntheses of seedlings using radioactive precursors.

1962-1963   Laboratory Assistant, Sloan Kettering Institute for Cancer Research, New York. Purification and preparation of compounds from gasoline exhaust and cigarette smoke by column and paper chromatography for the testing of these compounds for carcinogenic effects on mice.

IN-HOUSE SUPPORT STAFF

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: Edgar R. Stephens	SOCIAL SECURITY NO.:	BIRTHDATE: (Mo., Day, Yr.)
TITLE Professor of Environmental Science and Chemist	021-22-7438	Aug. 26, 1924

PLACE OF BIRTH (City, State, Country)	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.)
Detroit, Michigan, U.S.A.	U.S.

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
Carnegie Institute of Technology, Pittsburgh, Pa.	B. S.	1945	Chemistry
Princeton University, Princeton, N. J.	M. A.	1949	Chemistry
Princeton University, Princeton, N. J.	Ph.D.	1951	Chemistry

HONORS: Tau Beta Pi (1945); Sigma Xi (1949).

MAJOR RESEARCH INTEREST:	ROLE IN PROPOSED PROJECT:
Chemistry of Polluted Air	Consultant

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1963-present	Professor of Environmental Science, Soil Science and Agricultural Engineering Department and Chemist, Statewide Air Pollution Research Center, University of California, Riverside.
1959-1963	Scott Research Labs., Inc., Perkasie, Pa., and San Bernardino, Calif., Senior Chemist; (Research Associate at University of California, Riverside.)
1950-1959	Franklin Inst. Labs., Philadelphia Pa., Senior Staff Chemist.
1945-1947	Research Chemist, Shawingan Resins Corporation, Springfield, Mass.

Principal Fields of Interest: Chemistry and photochemistry of polluted air, analytical methods: infrared spectroscopy and gas chromatography, hydrocarbons, peroxyacyl nitrates, aerosols. Auto emissions.

Professional Memberships: American Chemical Society (Chairman, San Gorgonio Section, 1967); Air Pollution Control Association (Chairman, West Coast Section, 1970-1971); American Association for the Advancement of Science; Coblentz Society (Infrared).

Committees and Consulting: Scientific Committee, Riverside County Air Pollution Control District (1963, Vice Chairman); Inter Society Committee--Manual of Methods for Ambient Air Sampling and Analysis: Subcommittee No. 4, Carbon Compounds (1968-date); Consultant to: California Motor Vehicle Pollution Control Board, 1963; Environmental Protection Agency; various companies and trade associations; Reviewer of technical papers for various scholarly journals (Analytical Chemistry, Science, Environmental Science and Technology).

Edgar R. Stephens (Continued)

Selected Invited Scientific Lectures: Photochemical Air Pollution: A Review, 11th
   Academic Meeting of Japan Society of Air Pollution, Osaka, Japan, October 6,
   1970; Photochemical Air Pollution: Role of the Fluorocarbons, Symposium on
   Ecology and Toxicology of the Fluorocarbons, Andover, Mass., October 30, 1972;
   A Survey of Photochemical Smog, ACS Lecture Tour of the Pacific Northwest,
   October 25-28, 1971; Hydrocarbons in Polluted Air, Coordinating Research Council,
   Air Pollution Symposium, May 3, 1971; Solar Spectroscopy in Air Pollution, Sympos-
   ium on Remote Sensing of the Environment, NASA, Washington, D.C., June 10, 1970.

Selected Publications: Book Chapters

The Photochemical Olefin-Nitrogen Oxides Reaction
   E. R. Stephens; Chemical Reactions in the Lower and Upper Atmosphere, R. D. Cadle
   (ed.), Interscience, New York, 1961, p. 51.

The Formation, Reactions, and Properties of Peroxyacyl Nitrates (PAN's) in Photo-
chemical Air Pollution
   E. R. Stephens; Advances in Environmental Science and Technology, Vol. 1, J. N.
   Pitts, Jr., and R. L. Metcalf (ed.), John Wiley and Sons, Inc., New York, 1969,
   pp. 119-146.

Oxides of Nitrogen
   E. A. Schuck and E. R. Stephens; Advances in Environmental Science and Technology,
   Vol. 1, J. N. Pitts, Jr., and R. L. Metcalf (ed.), John Wiley and Sons, Inc., New
   York, 1969, pp. 73-118.

Hydrocarbon Reactivities and NO Conversion in Real Atmospheres
   E. R. Stephens; Chemical Reactions in Urban Atmospheres, C. S. Tuesday (ed.),
   American Elsevier Publishing Co., 1971, pp 45-59

Tentative Method of Analysis for Peroxyacetyl Nitrate (PAN) in the Atmosphere (Gas
Chromatographic Method)
   R. G. Smith, R. J. Bryan, M. Feldstein, B. Levadie, F. A. Miller, and E. R.
   Stephens; Methods of Air Sampling and Analysis, American Public Health
   Association, Washington, D.C., 1972, pp. 215-219.

Comparison of Synthetic and Smog Aerosols
   E. R. Stephens and M. A. Price; J. Colloid Interface Sci., 39, 272 (1972);
   Aerosols and Atmospheric Chemistry, G. M. Hidy (ed.), Academic Press, New York,
   1972.

Selected Research Papers

Further Developments in the Chemistry of the Atmosphere
   Proc. Amer. Petroleum Inst., 37 (III), 171 (1957)
   W. E. Scott, E. R. Stephens, P. L. Hanst, and R. C. Doerr

Photochemical Reaction Products in Air Pollution
   Proc. Amer. Petroleum Inst., 40 (III), 325 (1960); Intern. J. Air Water Poll.,
   4, 79 (1961)
   E. R. Stephens, E. F. Darley, O. C. Taylor, and W. E. Scott

Long Path Infrared Spectroscopy for Air Pollution Research
   Infrared Physics, 1, 187 (1961)
   E. R. Stephens

Edgar R. Stephens (Continued)

Absorptivities for the Infrared Determination of Peroxyacyl Nitrates
Anal. Chem., 36, 928 (1964)
E. R. Stephens

The Production of Pure Peroxyacyl Nitrates
J. Air Poll. Control Assoc., 15, 87 (1965)
E. R. Stephens, F. R. Burleson, and E. A. Cardiff

The Role of Oxygen Atoms in the Atmospheric Raction of Olefins with Nitric Oxide
Intern. J. Air Water Poll., 10, 793 (1966)
E. R. Stephens

Reactions of Oxygen Atoms and Ozone in Air Pollution
Intern. J. Air Water Poll., 10, 649 (1966)
E. R. Stephens

Analysis of the Atmosphere for Light Hydrocarbons
J. Air Poll. Control Assoc., 17, 147 (1967)
E. R. Stephens and F. R. Burleson

Sources and Reactivity of Light Hydrocarbons in Ambient Air
Proc. Amer. Petroleum Inst., Div. of Refining, 47, 466 (1967)
E. R. Stephens, E. F. Darley, and F. R. Burleson

The Marine Layer and Its Relation to a Smog Episode in Riverside, California
Atmos. Environ., 2, 393 (1968); Atmos. Environ., 3, 238 (1969) (Comment)
E. R. Stephens

Chemistry of Atmospheric Oxidants
J. Air Poll. Control Assoc., 19, 181 (1969)
E. R. Stephens

A Damaging Explosion of Peroxyacetyl Nitrate
J. Air Poll. Control Assoc., 19, 261 (1969)
E. R. Stephens, F. R. Burleson, and K. M. Holtzclaw

Distribution of Light Hydrocarbons in Ambient Air
J. Air Poll. Control Assoc., 19, 929 (1969)
E. R. Stephens and F. R. Burleson

Smog Aerosol: Infrared Spectra
Science, 168 (3939), 1584 (1970)
E. R. Stephens and M. A. Price

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: Roger Atkinson	SOCIAL SECURITY NO.: 560-15-8257	BIRTHDATE: (Mo., Day, Yr.) July 30, 1945
TITLE Assistant Research Chemist		

PLACE OF BIRTH (City, State, Country) Scarborough, England	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.) U.K.

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
Queens' College, University of Cambridge, U.K.	B.A.	1966	Natural Sciences
" " "	Ph.D.	1969	Physical Chemistry
" " "	M.A.	1970	Natural Sciences

HONORS:

MAJOR RESEARCH INTEREST: Photochemistry and reactions in the gas phase.	ROLE IN PROPOSED PROJECT:

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1972-present Assistant Research Chemist at University of California, Riverside. Research is being undertaken in the fields of $O(^3P)$-aromatics, O_3-olefins and other reactions of $O(^3P)$ and OH radicals. Using photoionization mass spectrometry (with Dr. K. D. Bayes at UCLA) the intermediates and products of the O_3-olefin reactions have been studied in a low pressure flow system.

1971-1972 Postdoctoral Fellow at York University, Downsview, under the supervision of Dr. K. H. Welge. Rates of deactivation of $O(^1S)$ atoms by CO_2, O_2, NO, N_2, and the noble gases were determined over the temperature range 200 - 450°K, using a flash photolysis-photon counting system. In addition, relative quantum yields of the photoproduction of $O(^1S)$ from N_2O, CO_2, O_3 and O_2 at the Lyman-α 1216 Å line were determined using a similar system.

1969-1971 Postdoctoral Fellow at National Research Council of Canada under the supervision of Dr. R. J. Cvetanovic. Rate constants for reactions of $O(^3P)$ and H atoms with NO and olefins were determined over the temperature range 280 - 500°K by a modulation-phase shift technique.

1966-1969 Thesis research at the University of Cambridge under the supervision of Dr. B. A. Thrush on the gas phase photoisomerisation of 1.3.5 cyclo-heptatriene, over the wavelength range 2288 - 3130 Å. The results were compared with modern treatments of unimolecular theory and average energies transferred per collision to various quenching gases were obtained.

Roger Atkinson (Continued)

Publications

Collisional Quenching in the Photochemical Isomerisation of 1.3.5 Cyclo-
heptatriene
    Chem. Phys. Letters, 3, 684 (1969)
    R. Atkinson and B. A. Thrush

Photochemical Studies of Unimolecular Processes, I. The Photoisomerisation of
Cycloheptatriene and Cycloheptatriene-d_8
    Proc. Roy. Soc., A316, 123 (1970)
    R. Atkinson and B. A. Thrush

Photochemical Studies of Unimolecular Processes. II. Isomerisation and
Quenching of Vibrationally Excited Cycloheptatriene
    Proc. Roy. Soc., A316, 131 (1970)
    R. Atkinson and B. A. Thrush

Photochemical Studies of Unimolecular Processes. III. Subsidiary Processes
in the Photolysis of Cycloheptatriene
    Proc. Roy. Soc., A316, 143 (1970)
    R. Atkinson and B. A. Thrush

Determination of the Absolute Values of the Rate Constants of the Reactions
of $O(^3P)$ Atoms with Alkenes by a Modulation Technique
    J. Chem. Phys., 55, 659 (1971)
    R. Atkinson and R. J. Cvetanovic

Vibrational Deexcitation of Highly Excited Polyatomic Molecules. The Amount
of Energy Transferred per Collision
    J. Phys. Chem., 75, 3376 (1971)
    B. S. Rabinovitch, H. F. Carroll, J. D. Rynbrandt, J. H. Georgakakos,
    B. A. Thrush and R. Atkinson

Activation Energies of the Addition of $O(^3P)$ Atoms to Olefins
    J. Chem. Phys., 56, 432 (1972)
    R. Atkinson and R. J. Cvetanovic

Temperature Dependence of the Deactivation of $O(^1S)$ by CO_2, O_2, N_2 and Ar.
    J. Chem. Phys., 57, 3689 (1972)
    R. Atkinson and K. H. Welge

Determination of the Rates of Hydrogen Atom Reaction with NO by a Modulation
Technique
    Can. J. Chem., In press
    R. Atkinson and R. J. Cvetanovic

Photodissociative Production of $O(^1S)$ from CO_2, O_2, O_3 and N_2O at the 1216 Å
Lyman-α Line
    J. Chem. Phys., In press
    B. A. Ridley, R. Atkinson and K. H. Welge

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: Karen R. Darnall	SOCIAL SECURITY NO.:	BIRTHDATE: (Mo., Day, Yr.)
TITLE Assistant Research Chemist	549-60-5865	Sept. 15, 1940

PLACE OF BIRTH (City, State, Country)	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.)
Rockford, Washington, U.S.A.	U.S.

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
University of California Los Angeles	B.S.	1962	Chemistry
University of Utah, Salt Lake City	Ph.D.	1969	Chemistry
University of California, Riverside	Postdoctoral	1969-71	Chemistry

HONORS:
PHS Air Pollution Special Postdoctoral Fellowship, 1969-71

MAJOR RESEARCH INTEREST: Organic chemistry and photochemistry of air pollution	ROLE IN PROPOSED PROJECT:

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1971-present   Assistant Research Chemist, Department of Chemistry and Statewide Air Pollution Research Center, University of California, Riverside. Continue study of chemical reactivity of peroxyacetyl nitrate.

1970-1971   Manager, Office of Educational Services, Statewide Air Pollution Research Center, University of California, Riverside.

1969-1971   PHS Air Pollution Special Postdoctoral Fellow with Professor J. N. Pitts, Jr., University of California, Riverside. Studied chemical reactivity of peroxyacetyl nitrate with olefins, mercaptans and sulfides in solution.

1967-1969   Research Assistant for Professor W. G. Bentrude, University of Utah, Salt Lake City. Thesis research on photochemistry of organophosphorus compounds and of biacetyl.

1965-1967   Research Assistant for Professor R. K. Robins, University of Utah, Salt Lake City. Synthesis and proof of structure of new and naturally occurring nucleosides.

1962-1965   Chemist, Research Division, Riker Laboratories, Northridge, Calif. Synthesis and proof of structure of a large variety of organic compounds including preparation of 10-25 g of analytically pure samples of each for biological testing (cancer).

Professional Memberships: American Chemical Society; The Chemical Society, London; Sigma Xi.

Karen R. Darnall (Continued)

Publications

3-β-D-Arabinofuranosyladenine
    J. Heterocyclic Chem., 3, 371 (1966)
    K. R. Darnall and L. B. Townsend

The Structure of Showdomycin, A Novel Carbon-Linked Nucleoside Antibiotic
Related to Uridine
    Proc. Nat. Acad. Sci., 57, 548 (1967)
    K. R. Darnall, L. B. Townsend and R. K. Robins

Photocondensation of Acetone with 2,2,2-Trimethoxy-4,5-dimethyl-1,3,2-
dioxaphospholene
    Tetrahedron Lett., 2511 (1967)
    W. G. Bentrude and K. R. Darnall

A Free-Radical Acylation
    J. Am. Chem. Soc., 90, 3588 (1968)
    W. G. Bentrude and K. R. Darnall

Biacetyl Photochemistry: Products in Solution
    Chem. Commun., 810 (1968)
    W. G. Bentrude and K. R. Darnall

Oxetan Intermediate in the Photocondensation of Acetone with 2,2,2-Trimethoxy-4,
5-dimethyl-1,3,2-dioxaphospholen
    Chem. Commun., 862 (1969)
    W. G. Bentrude and K. R. Darnall

The Base-Induced Decomposition of Peroxyacetyl Nitrate
    Tetrahedron Lett., 3765 (1969)
    R. P. Steer, K. R. Darnall and J. N. Pitts, Jr.

Peroxyacetyl Nitrate. A Novel Reagent for Oxidation of Organic Compounds
    J. Chem. Soc., D 1305 (1970)
    K. R. Darnall and J. N. Pitts, Jr.

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: John William Peters	SOCIAL SECURITY NO.: 557-60-0712	BIRTHDATE: (Mo., Day, Yr.) 5-4-43
TITLE		

PLACE OF BIRTH (City, State, Country) San Diego, California, U.S.A.	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.) U.S.

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
San Diego State College	B.S.	1965	Chemistry
University of California, Los Angeles	Ph.D.	1971	Organic Chemistry
University of California, Riverside	Postdoctoral Fellow	1971-73	Chemistry

HONORS:

See below

MAJOR RESEARCH INTEREST: Gas and Solution Phase Chemistry of Singlet Oxygen; Organic Reaction Mechanisms;Chemiluminescent Reactions	ROLE IN PROPOSED PROJECT: Assistant Research Chemist

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

HONORS: National Science Foundation Undergraduate Research Fellowship; du Pont Cash Award, Outstanding Graduating Senior, Dept. of Chemistry, San Diego State College, 1965; Graduated Summa Cum Laude, San Diego State College, 1965; Outstanding Teaching Assistant Award, Dept. of Chemistry, UCLA, Cash Award, 1969.

1973-present Assistant Research Chemist, University of California, Riverside

1971-1973 Postdoctoral Fellow, under direction of James N. Pitts, Jr., Department of Chemistry, University of California, Riverside. Performed research related to the chemistry of singlet oxygen (new sources and reactions) and studied the chemiluminescent reactions of peroxyacetyl nitrate (potential atmospheric monitor).

1966-1971 Research Assistant, under Professor C. S. Foote, University of California, Los Angeles. Performed research on the kinetics and mechanisms of the sensitized photooxidation of sulfides (Ph.D. dissertation).

John W. Peters (Continued)

Publications

The Reaction of Chloro-t-butyl Hydroperoxide with Base
     Tetrahedron Lett., 5, 531 (1966)
     W. H. Richardson, J. W. Peters, and W. Konopka

Quenching of Singlet Oxygen
     Ann. N.Y. Acad. Sci., 171, 139 (1970)
     C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters

Chemistry of Singlet Oxygen XIV: A Reactive Intermediate in Sulfide
Photooxidation
     J. Amer. Chem. Soc., 93, 3795 (1971)
     C. S. Foote and J. W. Peters

Photooxidation of Sulfides
     Pure and Applied Chem. (Suppl.), 4, 129 (1971)
     C. S. Foote and J. W. Peters

A New and Unique Source of Singlet Molecular Oxygen-Potassium Perchromate
     J. Amer. Chem. Soc., 94, 4348 (1972)
     J. W. Peters, J. N. Pitts, Jr., I. Rosenthal, and H. Fuhr

Chemiluminescent Reactions of Peroxyacetyl Nitrate and Ozone with
Triethylamine. A Possible Atmospheric Monitor of PAN
     Environ. Sci. Tech. (1972) (In Press)
     J. N. Pitts, Jr., H. Fuhr, J. S. Gaffney, and J. W. Peters

Sensitized Photooxidation of Sulfides
     Dissertation, UCLA (1971)
     J. W. Peters

BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 2, beginning with the Principal Investigator. Use continuation pages and follow the same general format for each person.)

NAME: Peter H. Wendschuh	SOCIAL SECURITY NO.:	BIRTHDATE: (Mo., Day, Yr.)
TITLE Postdoctoral Research Chemist	288-40-3315	May 27, 1944
PLACE OF BIRTH (City, State, Country) Wadsworth, Ohio, U.S.A.	PRESENT NATIONALITY: (If Non-U.S. Citizen, indicate kind of visa and expiration date.) U.S.	

EDUCATION: (Begin with baccalaureate and include postdoctoral)

INSTITUTION AND LOCATION	DEGREE	YEAR	SCIENTIFIC FIELD
The Ohio State University	B.Ch.E.-MS	1967	Chemical Engineering
University of California, Berkeley	Ph.D.	1971	Organic Chemistry

HONORS: Ohio State: Tau Beta Pi, Phi Lambda Upsilon, Phi Eta Sigma honoraries; President's Scholarship (4 yrs), United Oil Products Scholarship (1 yr). U.C. Berkeley: National Science Foundation Predoctoral Fellow (4 yrs)

MAJOR RESEARCH INTEREST: Organic Chemistry Photochemistry, Chemistry of Peroxyacetyl Nitrate	ROLE IN PROPOSED PROJECT: Assistant Research Chemist

RESEARCH AND/OR PROFESSIONAL EXPERIENCE: (Starting with present position, list professional background and employment.)

1972 - present Postdoctoral Research Chemist, Statewide Air Pollution Research Center, University of California, Riverside. Studied the reactions of peroxyacetyl nitrate and ozone with amines, with applications to atmospheric monitoring. Helped set up analytical laboratory for SAPRC smog chamber facility. Worked on joint NASA-UCR airborne monitoring program.

1971 - 1972 Environmental Sciences Postdoctoral Fellow, Department of Chemistry, University of California, Riverside. Studied the reactions of peroxyacetyl nitrate with various organic compounds, e.g. aldehydes and alcohols.

1967 - 1971 Research Assistant, Department of Chemistry, University of California, Berkeley. Studied the photochemistry of $\Delta^{2,4}$ - hexalin and its derivatives, resulting in a general theory about the factors controlling 1,3-cyclehexadiene photochemistry.

Professional Membership: Sigma Xi

UCR-RO Form P-170 (3/71)

Peter H. Wendschuh (Continued)

Publications:

Magnetic Circular Dichroism Investigation of Some Conjugated Olefins
    J. Org. Chem., 37, 1209 (1972)
    W. G. Dauben, J. Seeman, P. H. Wendschuh, G. Barth, E. Bunnenberg and
    C. Djerassi

The Photoequilibrium between 1,3-Cyclohexadienes and 1,3,5-Hexatrienes.
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